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• NUMBER THREE

RUBBER CHEMISTRY AND TECHNOLOGY

PUBLISHED QUARTERLY BY THE
DIVISION OF RUBBER CHEMISTRY
OF THE AMERICAN CHEMICAL SOCIETY





KOSMOS 60

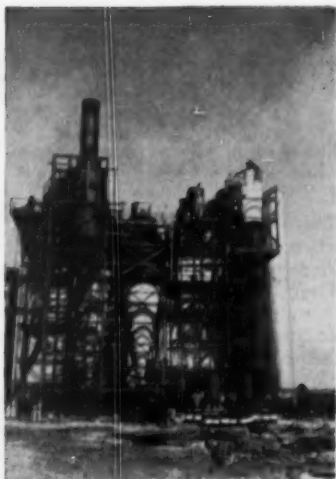
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The Philblacks are famous for their versatility. If you need a special characteristic in your finished product, a Philblack is right for your purpose. Your Philblack technical sales representative will be glad to help you. Call on him for information and assistance with your carbon black problems.

*A trademark



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Philblack I ISAF Intermediate Super Abrasion Furnace Black

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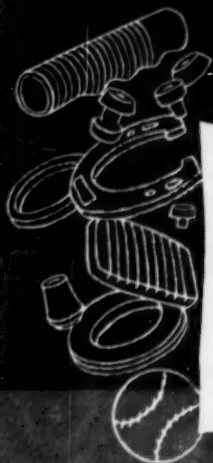
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Rubber Red PBD	Rubber Green GSD
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- Outstanding heat aging resistance
- Non-blooming in cured or uncured state
- High strengths at low concentrations
- Easy and uniform dispersion
- Good hot compression set
- Moderate price

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780 N. Clinton Avenue
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Please send me compounding information ☐
and a sample of VA-7 ☐

NAME _____ FUNCTION _____
COMPANY _____
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SYNTHETIC RUBBERS • PLASTICIZERS • CHEMICALS • ROCKET MOTORS

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wants to help with your rubber problems

Maybe you have used rubber compounds for years, or perhaps you're a comparative newcomer in the field. In either case, our laboratory and plant studies of various rubber compounds . . . their characteristics, advantages, behavior under different temperatures and varying conditions . . . can be of benefit to you.

In addition, our technical representative will be glad to help with *your special* rubber problems. Phillips practical experience with rubber, backed by the latest laboratory research and testing techniques, can help you use PHILPRENE more efficiently . . . and therefore more profitably. This service is free, of course.



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HOT	PHILPRENE 1000 PHILPRENE 1001 PHILPRENE 1006 PHILPRENE 1009 PHILPRENE 1018 PHILPRENE 1019 NOTE: PHILPRENE	
COLD	PHILPRENE 1500 PHILPRENE 1502 PHILPRENE 1503 1019 AND 1503 ARE ESPECIALLY DESIGNED FOR THE WIRE AND CABLE INDUSTRY	PHILPRENE 1601 PHILPRENE 1605—Philblack A cold rubber masterbatch
COLD OIL	PHILPRENE 1703 PHILPRENE 1706 PHILPRENE 1708 PHILPRENE 1712	PHILPRENE 1803 similar to GR-S 1801 but incorporating 25 parts Philrich [®] 5

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Rubber Chemicals Division, 318 Water Street, Akron 8, Ohio



Paul L. Day

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quality building
miracle additive?*

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hydrocarbon resins
to make better rubber
products, build
quality and cut costs!



Here are the facts!

PHYSICAL PROPERTIES	GE-9	AB-11-4	X-30
Type	Thermoplastic Hydrocarbon Solid or Powder	Thermoplastic Hydrocarbon Solid or Flaked	Thermoplastic Hydrocarbon Solid or Flaked
Form			
Specific Gravity @ 60°F	1.13-1.15	1.09-1.02	1.08-1.02
Weight per gallon @ 60°F (lbs.)	9.41-9.58	9.08-9.33	9.08-9.33
Bulking Value @ 60°F	0.1044-0.1052	0.1074-0.1102	0.1074-0.1102
Softening Point (Ball and Ring)	220°-230°F	220°-230°F	210°-220°F
Color (Coal Tar Scale)	20-22	3½-4½	1½-2*
Acid No.	0-2	0-2	0-2
Saponification No.	0-2	0-2	0-2

*Color: Gardner: 10-11; Rosin Scale: I-K.

These resins also have exceptionally good electrical insulation properties, because they are hydrocarbon polymers. Compatible with a variety of natural and synthetic rubber compounds.

FOR: battery cases, electrical insulation, rubber shoe soles and heels, rubber floor tiling, gaskets and jar rings, hard rubber compounds, tubular compounds, mechanical goods, rubber adhesives and cements, reclaimed rubber, molded rubber products, colored rubber stocks.

ADVANTAGES: better milling, calendaring, and tubing; more uniform cures, non-scorchy stocks; greater toughness, hardness, resistance to tearing, aging and abrasion; improved tensile strength and elongation; lower raw materials costs.

Write for
Technical Bulletin 218.

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HYDROCARBON RESINS!

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Compounds containing PANAREZ RESINS
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- Improved ozone resistance
- Improved tear resistance
- Improved tensile strength and elongation

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 Hydrocarbon drying oils

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The Problem: Produce GR-S/HAF black tread stock with maximum resistance to ozone under dynamic and static conditions.

Here's What Monsanto Compounds Did: Compounded a GR-S 1500/HAF black tread stock with Santoflex® AW alone and in combination with Flectol® H, Santoflex DD and three other commercial antioxidants. The stocks were also checked after the addition of paraffin.

The Results: Without exception, a stock with 2 parts of Santoflex AW proved most practical under dynamic or static exposure tests both in the ozone test chamber and in outdoor exposure. Paraffin was shown to add measurably to static ozone resistance without seriously harming the cracking under dynamic conditions.

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way we can sell. So call upon 30 years of experience in helping *chemically* to make rubber processing more efficient, rubber products better. If you think your tonnage is too small for a special research project, don't hesitate to talk it over with Monsanto. Among the 18,000 or so special reports—the answer to your problem may already be at hand. Just call, wire, or write: **MONSANTO CHEMICAL CO., Rubber Chemicals Dept. RC-2** (Telephone: HEMlock 4-1921), Akron 2, Ohio.

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Antioxidants • For maximum oxidation resistance.

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Odorless)
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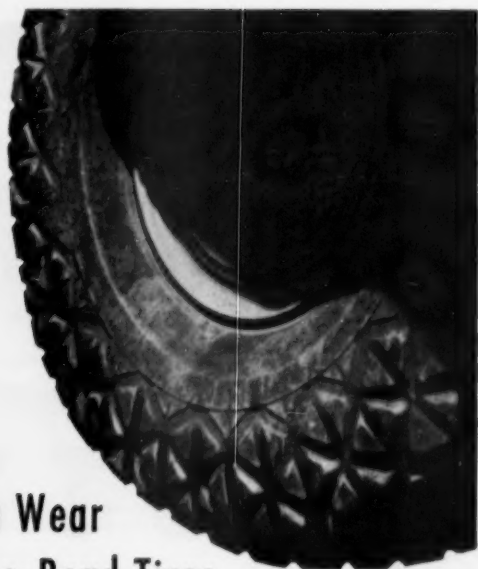
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OFF-THE-ROAD TIRES require the cut-and-chip resistance of Cabot's Vulcan 6 ISAF* or Vulcan 9 SAF** carbon blacks. For heavy duty tires that can withstand the roughest kind of off-the-road wear and tear, use Vulcan 6 or Vulcan 9 in your rubber compounds. Both blacks are recommended for the manufacture of tires used in mining, logging, oil field, construction, and all other off-the-road operations where the going is "rough and tough."

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*Vulcan 6 Intermediate Super Abrasion Furnace Black

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- Excellent adhesion is obtained to fabrics and metals.
- Thermal interaction of Butyl with carbon black improves properties such as abrasion and resilience.
- Non-staining grades of Enjay Butyl do

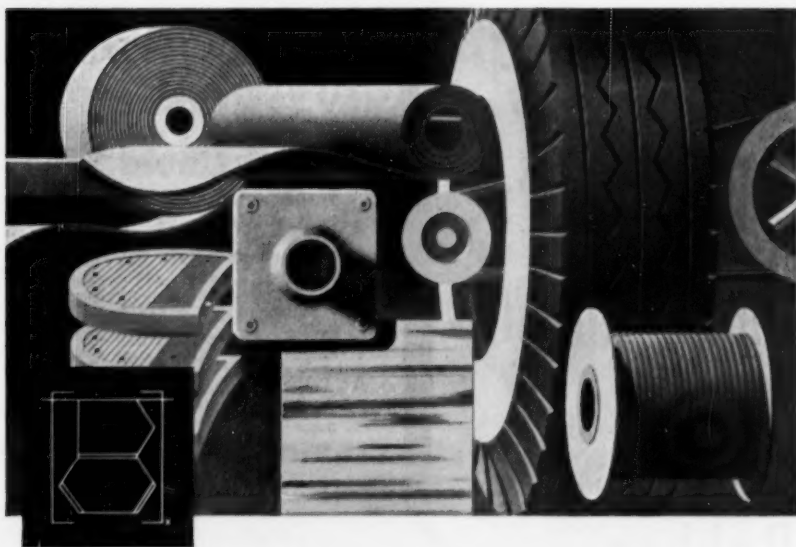
not fade or discolor on exposure to light or weather.

- Moldings and extrusions do not crack from sunlight or weather exposure and they retain new appearance and performance longer.
- Has excellent electrical properties plus resistance to ozone, corona, moisture absorption and abrasion, that is outstanding.
- Resists both heat and aging in high voltage insulation compounds.
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Division of United States Rubber Company
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Naugatuck Chemical

Division of United States Rubber Company
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JULY - SEPTEMBER • 1956

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AND TECHNOLOGY

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OF THE AMERICAN CHEMICAL SOCIETY



CARBON BLACKS

for RUBBER COMPOUNDING

ISAF (Intermediate Super Abrasion Furnace)
STATEX®125

HAF (High Abrasion Furnace)
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MPC (Medium Processing Channel)
STANDARD MICRONEX®

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RUBBER CHEMISTRY AND TECHNOLOGY

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July-September, 1956

No. 3

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 May 16.

FUTURE MEETINGS

Meeting	City	Hotel	Date
1956 Spring	Cleveland	Cleveland	May 16-18
1956 Fall	Atlantic City	Chalfonte-Haddon Hall	September 19-21
1957 Spring*	Montreal	Sheraton-Mt. Royal	May 15-17
1957 Fall	New York	Commodore	September 11-13
1958 Spring	Cincinnati	Netherlands Plaza	May 14-16
1958 Fall	Chicago	Sherman	September 10-12
1959 Spring	Buffalo	Statler	May 13-15
1959 Fall	Atlantic City	**	September 16-18

* Joint meeting with the Rubber Division of the Canadian Institute of Chemistry.

** Hotel not yet assigned by the American Chemical Society.

NEW BOOKS AND OTHER PUBLICATIONS

ENCYCLOPÉDIE TECHNOLOGIQUE DE L'INDUSTRIE DU CAOUTCHOUC. Vol-
 ume III. Edited by G. Génin and B. Morisson. S. R. L. Dunod, Paris.
 1956. Cloth, $6\frac{1}{2} \times 10$ inches, 614 pages.—This is the third volume of a four-
 volume work, and is the first of the four volumes to be published. Volume I
 will deal with the manufacture and properties of natural and synthetic rubbers,
 Volume II with compounding, compounding ingredients, and testing, and Vol-
 ume IV with pneumatic tires, inner tubes, and the direct use of latex.

The present volume includes rubber products other than tires and tubes and
 consists of twenty-four chapters: conveyor and transmission belting; hose;
 molded articles; bonding rubber and ebonite to metals; rubber rolls; extrusion
 and extruded products; expanded rubber; sponge rubber; ebonite; boots and
 shoes; soles and heels; proofed fabrics; flooring; wires and cables; tennis and
 golf balls; surgicals, sports and games; rubber thread; erasers; rubber-bonded
 abrasives; rubber jointing; elastic couplings and mountings; rubber in military
 protective equipment; industrial protective clothing; and adhesives.

Nearly every chapter is by a different author or authors, so that the book
 benefits from the specialized knowledge of the contributors.

As a whole the book embodies much useful material, particularly from the
 practical angle, and it is probably the most comprehensive work extant on
 rubber goods excluding tires and tubes, which will be included in Volume IV.
 [From the *Rubber Journal*.]

Volume IV. Edited by G. Génin and B. Morisson. 588 pages.—Volume
 IV is concerned with two subjects: tires and uses of latex. Under tires, the
 history, fabrication, techniques of testing, reinforcement, and repairing of tires
 are dealt with. Under latex, both natural and synthetic, chapters treating
 compounding ingredients, molding, sponge production, latex adhesion, latex
 paints, electric wires and cables, analyses, and testing are included, among
 others.

The articles were written mostly by French specialists in the field, based primarily on the operation and achievements of the French rubber industry. The intent of the work is to cover both the industrial and theoretical points of view. The volume is illustrated with photographs, graphs, and data tables. [From the *Rubber World*.]

POLYMER PROCESSES. Edited by C. E. Schildknecht. High Polymers, Volume X. New York and London: Interscience Publishers, 1956, xvii+914 pp. 156s. 0d. net; 158s. 0d. post free.—This further volume in the series is concerned with the preparation, formulation and processing of plastics, synthetic rubbers, fibers and adhesives, with special emphasis on recent techniques, and has been written particularly with a view to bridging the gap between theory and practice. The book is the work of twenty contributors, fifteen from the USA, two from Sweden, and one each from England, Canada and Germany. The editor, C. E. Schildknecht, of the Stevens Institute of Technology, Hoboken, N. J., is also one of the contributors.

The first six chapters are devoted to various methods of polymerization—free radical polymerization, ionic polymerization and polymerization in bulk, in suspension, in emulsion and in solution. The subjects of the remaining twelve chapters are as follows: Polyamides and polyesters; condensations with formaldehyde; cellulose and cellulose derivatives; epoxy resins; polysulfide polymers; new adhesives; stabilization of polymers; polymer pastes; polymer latexes; compounding and processing of synthetic rubbers and resins; reinforcement of polymers; and spinning and drawing of synthetic fibers. The book contains many hundreds of references to literature and patents.

The three chapters likely to be of greatest interest to rubber technologists are those on (1) compounding and processing of synthetic rubbers and resins, by G. S. Garvins of the B. F. Goodrich Chemical Co.; (2) polysulfide polymers, by E. M. Fettes and J. S. Jorczak, of the Thiokol Chemical Corporation; and (3) polymer latexes, by G. J. Antlfinger and N. H. Sherwood, of the B. F. Goodrich Chemical Co. Several pages are devoted to rubber-resin adhesives. Emulsion polymerization occupies a 60-page chapter by H. L. Williams of Polymer Corporation, Ltd., several hundred copolymers, as well as homopolymers and terpolymers, which have been prepared in emulsion systems being listed. [From the *Rubber Journal*.]

PRÜFUNGSBUCH FÜR KAUSCHUK UND KUNSTSTOFFE. Edited by K. Frank. Stuttgart: Berliner Union G.m.b.H., 1955, pp. 119. DM18; 36s. 0d. post free from London.—This handy volume is a survey of methods and apparatus for physical testing and is chiefly, although not exclusively, concerned with German equipment. Nearly half the book is devoted to vulcanized rubber and covers both static and dynamic mechanical testing, electrical testing, accelerated aging tests and the testing of ebonite. The two other principal sections of the book deal with the testing of raw rubber and of plastic films, while there are three short sections covering the testing of compounded unvulcanized rubber and finished rubber products, and instruments for optical tests. A list of ASTM and German DIN standards for testing rubber and a bibliography of 165 references to books and articles on the subject of rubber testing are included. The book is well produced and is liberally illustrated with over a hundred clearly reproduced photographs and diagrams. English readers will find the book useful as a source of information on German test methods and apparatus. [From the *Rubber Journal*.]

RUBBER IN AUTOMOBILE ENGINEERING. By R. Dean-Averns. Published by the Natural Rubber Development Board, London, England. Available in the U. S. from the Natural Rubber Bureau, 1631 K St., N.W., Washington 6, D. C. $5\frac{1}{2} \times 8\frac{1}{4}$ in. 216 pp. 75c.—This new book by the noted British automotive engineer R. Deans-Averns is one of the most comprehensive on the subject ever published. The author compiles in one volume a cross-section of detailed information that has work-a-day value for every automotive engineer. Over 100 illustrations and diagrams supplement the text. The book, which is a survey of the numerous uses of rubber in the automobile, with special emphasis on design considerations, gives a complete summary of the uses of rubber in the automobile industry, from the theoretical principles of construction to examples of their application in many different makes of vehicles. The author covers such aspects as engine vibration problems; suspension systems; the pneumatic tire; rubber in units attached to the body or frame; rubber in electrical fittings, hose, seals, etc.; rubber in body building and mounting; rubber in door mounting, glazing, panels, flooring, and seating. [From the *Rubber Age of New York*.]

THE PETROLEUM ACIDS AND BASES. H. L. Lochte and E. R. Littmann. London: Constable and Co., Ltd., 1955, pp. 368. 50s. Od. net.—Naphthenic products are used in various ways connected with the rubber industry—for example, the acid is an intermediate in the manufacture of rubber chemicals, copper naphthenate is used as preservative for textiles, and naphthenic oils are used as processing aids and reclaiming oils. For this reason, therefore, a book about naphthenic acids and petroleum bases should have some interest within the industry, although the approach is based mainly on the separation and chemistry of the products rather than on their applications.

The main part of the monograph was written by Dr. Lochte, who, as Professor of Chemistry at the University of Texas, is closely connected with the laboratory where most of the known naphthenic acids and all the known petroleum bases were isolated and identified. The chapters on the commercial isolation and applications of naphthenic acids were contributed by Littmann, of the Enjay Company, Inc. The book has additional value in that, as far as the petroleum bases are concerned, it is the first time that any attempt has been made to collect together the known facts about these materials.—B.J.W. [From the *Rubber Journal*.]

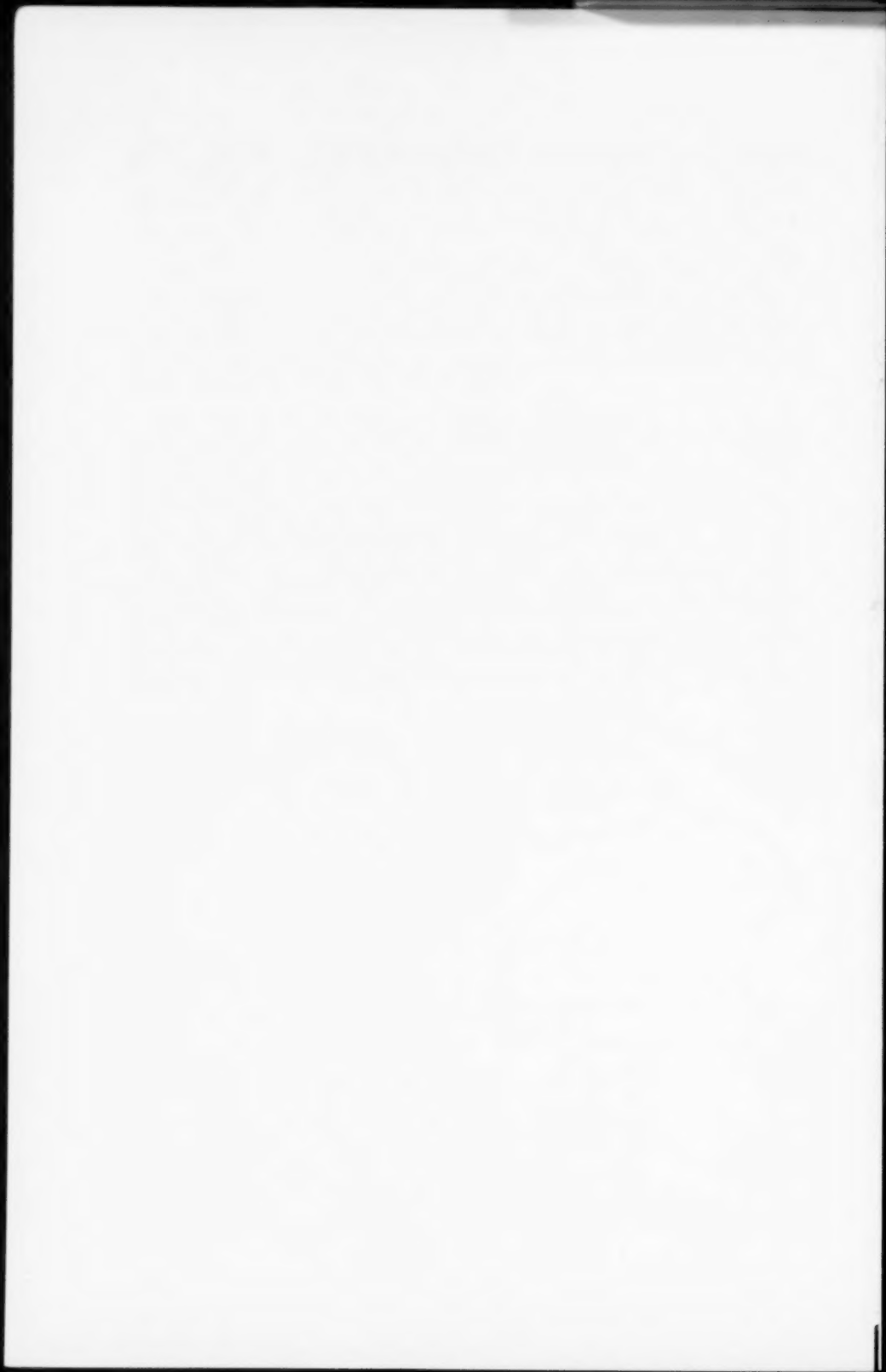
ASTM STANDARDS ON TEXTILE MATERIALS. 1956 Edition. American Society for Testing Materials, Philadelphia, Pa. 788 pages. Price, \$5.75.—The latest ASTM tentative and standard methods of test, specifications, and definitions pertaining to textile materials are included in this volume. Of the 118 standards and tentatives, 22 are new or revised since the last edition. Thirteen appendixes cover several proposed methods and recommendations. [From the *Rubber World*.]

THE SYSTEMATIC IDENTIFICATION OF ORGANIC COMPOUNDS: A LABORATORY MANUAL. (4th Edition.) By Ralph L. Shriner, Reynold C. Fuson, and David Y. Curtin. Published by John Wiley & Sons, Inc., 440 Fourth Ave., New York 16, N. Y. $5\frac{1}{2} \times 8\frac{1}{4}$ in. 448 pp. \$6.00.—The latest edition of this book includes reliable procedures for the preparation of numerous useful derivatives of organic compounds, as well as up-to-date discussions of the most important types of organic reactions. To this edition, however, the authors have

added a new chapter on infrared and ultraviolet spectroscopy, giving full indications for their use with the common functional groups. The discussion of reaction mechanisms has also been greatly revised and newer theories employed extensively in the treatments of relative reactivities, physical properties, and "solubility" behavior. Subjects covered in the present edition include the identification of unknowns, preliminary examination, determination of physical properties, qualitative analysis for the elements, the solubility classes, application of classification tests, use of spectroscopic methods for functional group determination, the preparation of derivatives, tables of derivatives, the separation of mixtures, and introduction to the solution of structural problems. The book has 13 chapters plus an appendix and a cross-referenced subject index. [From the *Rubber Age* of New York.]

THE VAN NOSTRAND CHEMIST'S DICTIONARY. Edited by J. M. Honig, M. B. Jacobs, S. Z. Lewin, W. R. Minrath, and George Murphy. D. Van Nostrand Co., Inc., New York, N. Y. Cloth, 6 × 9 inches, 765 pages. Price, \$10.—Planned to meet the needs of the chemist and the engineer, this dictionary contains more than 11,000 definitions of laws, equations, reactions, tests, solutions, laboratory apparatus, industrial processes, and equipment. Items are listed by both their proper names and common names for quick identification. The definitions are in accordance with the latest ACS nomenclatures and are systematically organized under a key-word plan that helps in cross-referencing the subjects. Here each word in a specific definition that is further defined elsewhere in the book is printed in bold-face type. This plan permits the reader to correlate all information from the various sciences on a specific point, thus providing a well-rounded, integrated knowledge of the subject. [From the *Rubber World*.]





CORAL RUBBER—A CIS-1,4-POLYISOPRENE

F. W. STAVELY AND COWORKERS*

THE FIRESTONE TIRE & RUBBER CO., AKRON, OHIO

For over one hundred years scientists have been endeavoring to produce a synthetic rubber having the polymer structure and physical properties of natural Hevea rubber.

Our present synthetic rubber industry is based primarily on a copolymer of butadiene and styrene; however, polyisoprenes and copolymers containing isoprene have not been overlooked.

GR-S type rubbers are now extensively used and give an excellent account of themselves in passenger tires and other products. It has, however, been generally recognized that these polymers are lacking in certain properties when compared to natural rubber. The more obvious of these deficiencies are high hysteresis, low gum tensile strength, and poor retention of physical properties, such as tensile strength, at elevated temperatures. Thus, great effort was expended in the government-sponsored synthetic rubber program to improve these characteristics.

The limited improvement obtained from the very extensive studies made of emulsion polymerization systems, monomers, monomer ratios, and copolymers directed our attention to other polymerization systems. It was observed that polymer structure could be influenced more readily by means of ionic polymerization systems with metal catalyst than by emulsion polymerization.

Therefore, a major objective was to find ways and means of making a polymer that would be similar chemically and structurally to natural rubber. It was anticipated that, if such a structure could be achieved, then we might expect the physical properties to be similar to those of natural rubber. Substantial progress has been made in developing a polymer having these characteristics.

The term "Coral rubber" is used as a convenience in identifying these rubberlike polymers and was suggested by the physical appearance of the polymers when formed under certain conditions.

SYNTHESIS OF CORAL POLYMERS

Isoprene purification.—Isoprene of high purity is purified further just prior to use by refluxing over sodium for 4 hours, followed by simple distillation; it is then passed through a silica column just prior to use. The isoprene is kept out of contact with air or moisture throughout the purification and polymerization process. The air or oxygen on the silica is removed by use of a stream of helium, free from oxygen.

* As coworkers of the senior author, the following were concerned in six different fields of activity in the entire project: *Polymerization*—R. F. Dunbrook, L. E. Forman, F. C. Foster, R. S. Stearns, T. B. Talcott, and L. B. Wakefield. *Rubber Technology*—G. Alliger, J. R. Russell, S. Smith, W. A. Smith, and J. M. Willis. *Microstructure*—J. L. Binder, M. J. Forster, E. E. Hanson, J. W. Liska, and H. C. Ransaw. *Macrostructure*—M. Barzan, R. D. Gates, and B. L. Johnson. *Pilot Plant*—J. P. Downing, C. H. Hammond, E. S. Hanson, C. G. Mayes, A. Para, and F. M. Smith. *Analysts*—M. J. Brock and K. C. Eberly. This paper is reprinted from *Industrial and Engineering Chemistry*, Vol. 48, No. 4, pages 778-783, April 1956. The paper was presented before the Division of Rubber Chemistry of the American Chemical Society at its meeting in Philadelphia, November 2-4, 1955.

Catalyst preparation.—The lithium metal catalyst is prepared by melting the metal immersed in vaseline or petroleum jelly and subjecting the molten mass to high-speed agitation in a specially designed apparatus. The entire operation must be carried out in a closed system under an atmosphere of inert gas (helium) and the container should be of stainless steel. The high speed stirrer is operated at 18,000 r.p.m. for about 30 minutes at 200° C.

The catalyst is generally made as a 35 per cent dispersion consisting of metal particles having a mean diameter of 20 μ or a surface area of about 1 square meter per gram. The vaseline which serves as a dispersing medium also protects the catalyst, which is highly pyrophoric.

Lithium appears to be unique as a catalyst in the polymerization of isoprene in that it strongly favors the formation of *cis*-1,4-structure (with a trace of 3,4-) to the exclusion of *trans*-1,4- and 1,2-structural arrangements, while metals, such as sodium, potassium, cesium, and rubidium give primarily mixtures of *cis*- and *trans*-1,4-, 1,2-, and 3,4-structures.

Polymerization.—Over 4000 pounds of Coral rubber has been produced in 50-gallon reactors by various procedures. A simple recipe is as follows:

Isoprene, parts	100.0
Lithium, part	0.1
Temperature	30–40° C

Coral polymers can be made in the laboratory in (dry) glass bottles sealed with aluminum-lined crown caps. The catalyst dispersion may be added to the bottle by weight and the monomer by volume. The cap is placed loosely on the bottle and the monomer brought to a vigorous boil by placing on a heated sand bath. When 10 per cent of the charge has been vented, the bottle is rapidly sealed. This procedure, while generally satisfactory, does not give the reproducibility that can be obtained in closed systems where air and moisture can be excluded.

The sealed bottle is placed on a wheel, immersed in water at constant temperature, and rotated. After an induction period, the charge goes through a period of thickening and finally becomes solid. The reaction continues for some time after the solid stage has been reached. At the end of the polymerization, all the monomer has been consumed, and there is a partial vacuum in the bottle. Alternatively, the charged bottle may be allowed to stand stationary in a constant-temperature bath until polymerization is complete. Ordinarily the static system requires a considerably longer time but is less hazardous.

After polymerization has been completed, the cooled bottle is cut open and the polymer removed and soaked in isopropyl alcohol containing antioxidant and acetic acid to remove the catalyst. Three per cent of polymerized trimethyldihydroquinoline (Agerite Resin D) is added on a wash mill as antioxidant. Water washing is resumed after addition of the antioxidant. The washed polymer is sheeted out and dried in vacuo in an oven at 50° C. The dried polymer is stored in polyethylene bags.

Our first laboratory polymer, free from *trans*-1,4-structure and high in *cis*-1,4-structure, was available for some time before its reproduction was attempted in the pilot plant. Early pilot plant work was conducted in vapor phase at 60° to 80° C to minimize hazards and to control temperature. In order to use lower temperatures we changed to static liquid-phase procedures and were able to reduce the temperature to about 50° C. We then changed to agitated liquid-phase techniques and were able to reduce the temperature to 40° C. It now appears that the best procedure for producing mass polymers may be to

initiate the reaction at 40° to 50° C until a decided thickening of the liquid occurs, and then reduce the temperature. Once the initiation reaction has taken place, the propagation reaction may continue at lower temperatures and can be strongly exothermic during the latter stages. If not properly controlled the heat evolved may degrade the polymer; it can be sufficient to cause charring.

It appears currently that the important factors influencing the structure of the polymer are the purity of the components, the exclusion of moisture, oxygen or air, and oxygen-containing materials. As the purity of the monomer increases, it becomes much more reactive, even with traces of catalyst, and the reaction often proceeds with explosive violence.

Coral Polymer Stability.—Coral polymer, containing antioxidant, is more light sensitive in the unvulcanized state than Hevea rubber. A surface softness develops rather quickly when Coral polymer is exposed to direct sunlight. A somewhat similar condition develops on exposure to diffused light for longer periods.

Although 3 per cent of Agerite Resin D is being used as a polymer stabilizer, it is not very effective as a light stabilizer. Other antioxidants and combinations of materials have not given as good light stability as that of natural rubber. A number of antioxidants appear to give good polymer stability when protected from light. For example, fifteen different Coral polymers, stabilized with 1 per cent of Santoflex BX (85 parts of 1,2-dihydro-2,2,4-trimethyl-6-phenylquinoline with 15 parts of *N,N'*-diphenyl-*p*-phenylenediamine) showed no appreciable change in Williams plasticity after aging in the dark for 1 year and 10 months.

The thermal stability of Coral polymer and compounded stocks appears to be better than that of natural rubber. When $\frac{1}{8}$ -inch cubes of Hevea and Coral stocks, containing 50 parts of a reinforcing carbon black (HAF), are heated for 1 hour in a molten metal bath¹ at temperatures from 170° to 270° C, the Hevea blocks begin to decompose at 165° C, about 30° C lower than the Coral blocks. When Coral rubber and Hevea rubber are heated in a vacuum at 200° C, the rate of rupture of the Coral chain is significantly less than that of Hevea. The rates of degradation of Coral and Hevea were compared by the method of Wall, Brown, and Hart².

POLYMER STRUCTURE

Macrostructure.—Coral rubber has been polymerized in the laboratory and pilot plant to an average molecular weight equivalent to or higher than that of the best grade of natural rubber. The molecular-weight distribution in Coral rubber is similar to that found in natural rubber. As a rule, mass polymerization at low temperature (0° C) produces polymers having very low gel content and high inherent viscosity. The molecular-weight distributions and molecular weight on breakdown are given in Tables I and II.

Microstructure.—The amounts of *cis*- and *trans*-1,4-, 1,2-, and 3,4-addition structures in Coral rubber were determined by an infrared spectroscopic method developed in these laboratories. The intensities of bands at 8.84, 8.68, 10.98, and 11.25 microns are measured to determine the amounts of the four types of additions, in the order given. The amounts of Hevea and balata in mixtures of various compositions can be determined by using the peak of a band at 8.84 microns for Hevea (*cis*) and at 8.68 microns for balata (*trans*), respectively. In Coral rubber there is no band at 8.68 microns and thus no *trans*-1,4-addition structure. The infrared spectra of films of Coral and Hevea rubber, illustrated

TABLE I
MOLECULAR-WEIGHT DISTRIBUTION OF CORAL VS. NATURAL RUBBER

	Acetone extract	Polymer in each inherent viscosity range (%)											Gel
		0-2*	2-4	4-6	6-8	8-10	10-12	12-14	14-16	16-18	18-20	Over 20	
Pale crepe	3.6	3.7	6.0	7.4	7.2	11.7	27.0	7.2	—	—	—	—	26.2
Dead-milled† natural rubber	3.3	30.0	53.5	—	—	—	—	—	—	—	—	—	12.8
Coral polymer													
RS-88, at 0° C	3.0	3.0	7.0	9.4	11.2	9.9	6.1	23.0	—	—	—	—	27.4
CPP-1224 at 40° C	3.1	1.9	10.4	11.9	16.4	—	—	—	—	—	—	—	56.3
CPP-1224 after 3-min. milling	3.1	11.0	30.1	46.6	11.7	—	—	—	—	—	—	—	1.5
CPP-1352 at 30° C	5.0	0.7	1.7	2.7	4.4	6.3	8.2	43.0	9.8	2.6	1.6	5.6	8.4

* Completely broken down.

† Viscosity range.

TABLE II
BREAKDOWN CHARACTERISTICS OF CORAL AND NATURAL
RUBBER ON MILLING

	Degree milled	Inherent viscosity after purification ^a	No. av. mol. wt. ^b
Coral (A5-I), 50° C	None	7.0	669,000
	20 pass	2.2	230,000
	Complete breakdown (dead-milled)	1.7	178,000
Smoked sheet	None	7.4	680,000
	20 pass	2.8	265,000
	Complete breakdown (dead-milled)	1.6	141,000

^a Polymer recovered after precipitation from toluene solution with 33% by volume of methanol.

^b Osmotic pressure measurement¹.

in Figure 1, show that the two substances are very similar. The similarity of Coral and Hevea rubber is further evident from the differential infrared spectra of Figure 2. In this comparison the cell containing Hevea in carbon disulfide solution is the standard. The structural differences in the experimental polymers are shown as deviations from the straight line at 100 per cent transmittance. Transmittance of less than 100 per cent results from those structural features in which the experimental polymer predominates and transmittance of more than 100 per cent from those in which Hevea predominates.

The microstructures of several Coral rubbers, recorded in Table III, are typical of many individual polymers that have been analyzed by this procedure. The *trans*-1,4-configuration and 1,2-addition are absent in all these polymers.

X-Ray Diffraction Evidence of Coral Rubber Microstructure.—Coral rubber exhibits the characteristic x-ray diffraction pattern of Hevea rubber, which

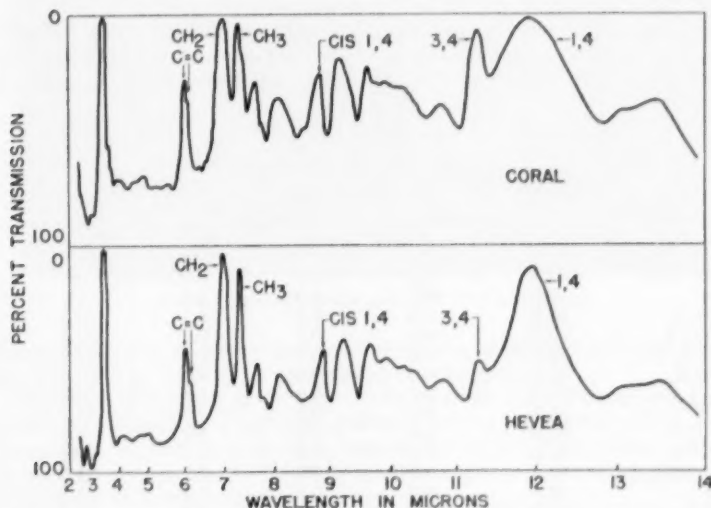


FIG. 1.—Infrared spectra of Coral and Hevea rubber films.

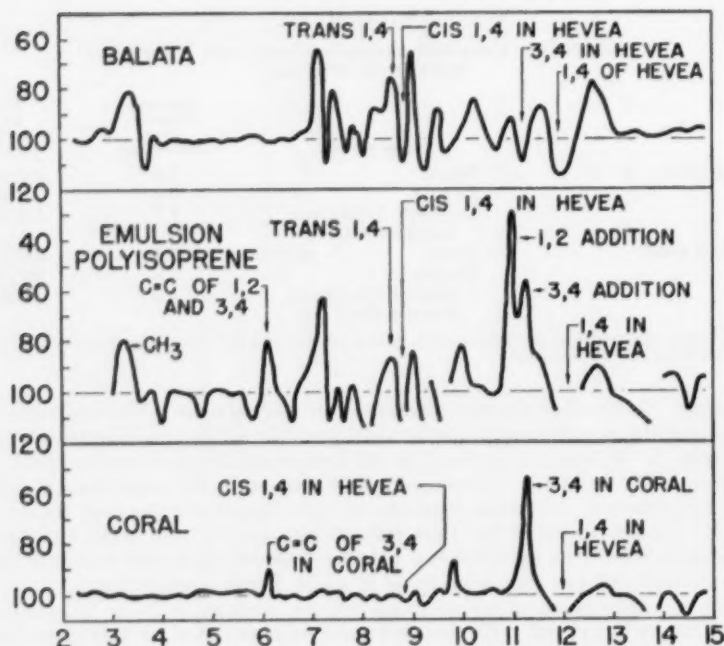


FIG. 2.—Differential infrared spectra of other polyisoprenes vs. Hevea.

indicates a striking similarity in the microstructures of the crystalline components.

All x-ray diffraction fiber patterns obtained for Coral rubbers are identical, except for intensity. Therefore, it is concluded that the crystalline component of the stretched Coral polymers has primarily a head-to-tail sequence of *cis*-1,4-

TABLE III
MICROSTRUCTURES OF POLYISOPRENES
(Based on Hevea 97.8% *cis* 1,4- and 2.2% 3,4-)

	Distribution of double bonds (%)				Unsaturation determined (%)
	<i>Cis</i> -1,4-	<i>Trans</i> -1,4-	1,2-	3,4-	
Hevea	97.8	0.0	0.0	2.2	—
Balata	0.0	98.7	0.0	1.3	—
RS-104-A	93.8	0.0	0.0	6.1	92.1
RS-105-12	93.4	0.0	0.0	6.5	89.5
RS-110-6	92.8	0.0	0.0	6.5	91.3
RS-118-F	93.4	0.0	0.0	6.0	97.4
1552	93.6	0.0	0.0	6.4	94.8
1557-R	94.1	0.0	0.0	5.9	91.7
CPP-1029	91.3	0.0	0.0	8.6	96.7
CPP-1188	91.5	0.0	0.0	8.4	90.3
CPP-1428R	92.9	0.0	0.0	7.5	91.5
RS-85-1	92.5	0.0	0.0	7.4	91.1
RS-99-B	93.7	0.0	0.0	6.3	91.2
CPP-1469	93.0	0.0	0.0	6.9	89.9

units, as in natural rubber. The maximum percentage crystallinity of elongated Hevea has been reported to be about 40 per cent⁴. We find the crystalline component of Coral rubber (when elongated to 1000 per cent) to be 25 per cent (Figure 3).

Numerous Coral polymers have been obtained which have a powder pattern at zero elongation similar to the pattern obtained with Hevea. Compared to

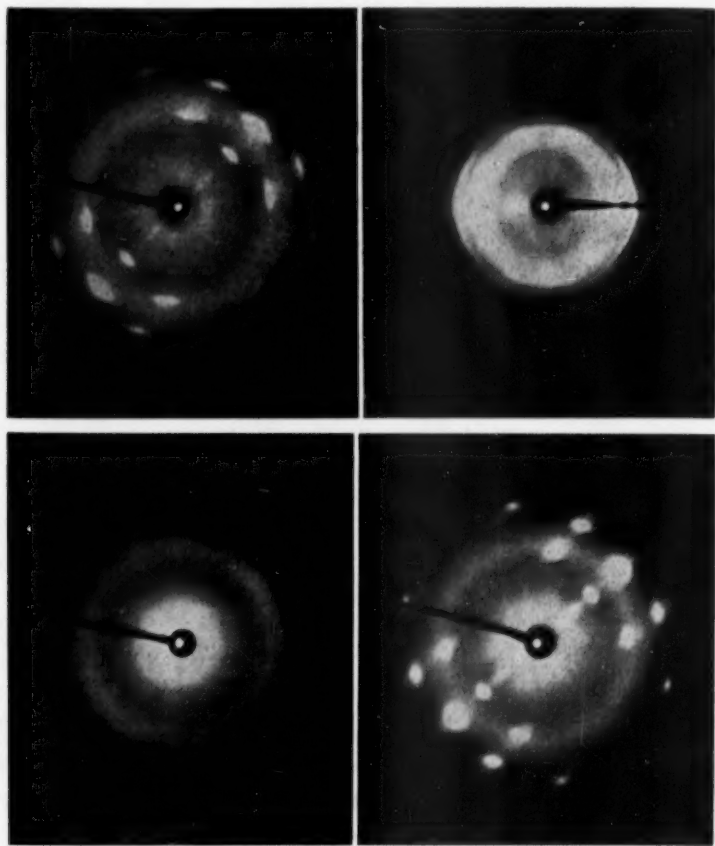


FIG. 3.—X-Ray diffraction patterns of stretched polymers.

Hevea, the Coral polymers generally require a considerably longer exposure time at -25° to -40° C to develop the powder pattern.

Chemical Evaluation of Structure.—Because of difficulties encountered in consistently obtaining a crystalline x-ray pattern with Coral rubber at zero elongation, the question arose as to whether this might be due to nonhomogeneous polymer structure or to the absence of certain nonrubber components normally present in Hevea rubber.

Ozonolysis results indicated that the amount of head-to-tail structure in

TABLE IV
OZONOLYSIS
(Temperature, -25°C to -14°C)

	Milled pale crepe	Coral	
		RS-99	CPP- 1356
Isolation of significant building blocks ^a (%)	86.24	76.42	80.43
Recovery of carbon originally present (%)	89.52	82.65	86.20
Head-to-head structure (%)	0.18	0.36	0.55
Head-to-tail structure (%)	98.06	92.86	94.67
Tail-to-tail structure (%)	1.7	6.78	4.78

^a Recovery of units that form succinic or levulinic aldehyde, hemialdehyde and (or) acid and 2,5-hexanedione.

TABLE V
POLYMER FEATURES

	Hevea	Coral				
		CPP- 1469	CPP- 1478	CPP- 1484	CPP- 1481	CPP- 1504
Inherent viscosity (unmilled)	—	11.6	13.9	12.5	9.7	6.1
Structure (%)						
<i>Cis</i> -1,4-	97.8	93.0	87.6	92.4	91.8	89.8
<i>Trans</i> -1,4-	0	0	3.2	0	0	1.7
3,4-addition	2.2	6.9	9.2	7.6	8.1	8.5

Physical Properties (Gum Stock)

ACS No. 1 Formula plus 1 part Santoflex BX, cured at 260°F

Minutes	Modulus at 600% elongation (lb./sq. in.)					
30	875	100	175	175	200	200
45	1100	200	225	200	225	275
60	1325	225	200	200	200	300
	Tensile strength (lb./sq. in.)					
30	3075	2225	2675	2475	2650	3400
45	3375	2650	3100	2575	3300	3425
60	3450	2750	3125	2825	3100	2600
	Elongation at break (%)					
30	790	950	1150	1020	1040	1100
45	770	920	1040	980	990	1000
60	750	900	1020	940	940	920

ACS No. 2 Formula plus 1 part Santoflex BK minus 0.5 part sulfur, cured at 260°F

Minutes	Modulus at 600% elongation (lb./sq. in.)					
30	525	150	200	250	200	125
45	850	225	275	400	400	200
60	1200	400	425	525	500	200
	Tensile strength (lb./sq. in.)					
30	2500	2350	3125	3075	2975	2475
45	3300	2975	2925	2950	3100	3100
60	3400	3275	2325	2850	2575	3300
	Elongation at break (%)					
30	800	980	1020	900	940	1120
45	780	900	920	840	880	980
60	750	860	810	780	780	920

Coral was comparable to that in Hevea (Table IV) by this method, but there is some indication of a small amount of tail-to-tail and head-to-head structure.

The number of internal double bonds (total *cis*- and *trans*-1,4-configuration) in Hevea and Coral were also compared by a method⁴, based on the difference in the rates of reaction of perbenzoic acid with internal and with external (1,2- or 3,4-addition) double bonds. These data show Hevea to be 97.1 per cent 1,4-configuration as compared to 94.3 per cent 1,4-configuration in Coral rubber. Total unsaturation was determined by the iodine monochloride method and found to be 96 per cent for Hevea compared with 98 per cent for Coral rubber.

PROCESSING CORAL RUBBER

When the Banbury internal mixer is used to break down Coral rubber, the time required is influenced by the original inherent viscosity and per cent gel in the polymer. No difficulty has been encountered in calendering Coral factory stocks. Sticking to the factory warm-up mill and calender rolls was prevented

TABLE VI
COMPARISON OF CORAL POLYMER WITH LTP AND
NATURAL RUBBER IN A GUM RECIPE

Cure at 280° F (minutes)	Natural rubber	LTP		Coral polymer
		600% Modulus (lb./sq. in.)		
30	775	50	225	
60	1000	150	300	
90	1100	125	300	
		Tensile strength (lb./sq. in.)		
30	3225	275	1925	
60	3125	250	3000	
90	2850	225	2400	
		Elongation at break (%)		
30	820	1000	1160	
60	760	740	1060	
90	700	700	990	

by adjusting the roll temperatures to 160° to 200° F. Careful control of the calender operation resulted in smoothly calendered sheets. Calendered Coral rubber body stocks have good tack. The same precautions of protection from light and heat that are used with natural rubber should be taken when storing Coral polymers or mixed stocks.

VULCANIZATE PROPERTIES

Coral Gum Stocks.—The tensile strength of Coral gum stocks approaches that of natural rubber. Values of 3000 to 3400 pounds per square inch are obtained with Coral rubber, whereas the average natural-rubber values generally fall in the range 3200 to 3700 pounds per square inch. The optimum gum tensiles for Coral rubber occur at higher elongation than those of natural rubber, and the modulus at 600 per cent elongation is lower.

Considerable variations occur in gum tensile values from polymer to polymer, the reason for which is not fully understood. These variations do not appear to be related to inherent viscosity or polymer structure. High tensile values (above 3000 pounds per square inch) can be obtained with most Coral

polymers by adjustment of the sulfur, accelerator ratios, and stearic acid content. The effect of two different formulations is apparent from the data in Table V.

The greatly improved tensile strength of the Coral rubber gum vulcanizate when compared to that of low-temperature butadiene-styrene copolymer (LTP) is evident from the data of Table VI.

TABLE VII
COMPARISON OF HEVEA, CORAL, AND LTP IN
35-PART EPC STOCKS

	Hevea	Coral	LTP
Inherent viscosity	—	5.2	—
Gel (%)	—	11.0	—
300% Modulus (lb./sq. in.)			
Cure at 280° F (minutes)			
30	750	325	300
45	900	375	550
60	1000	400	700
90	1100	425	—
Tensile strength (lb./sq. in.)			
30	3950	3575	3275
45	4350	3625	3650
60	4275	3775	3800
90	4300	3800	—
Elongation at break (%)			
30	720	840	820
45	670	800	780
60	630	800	660
90	600	790	—
Properties at 212° F			
Ring tensile strength (lb./sq. in.)			
45	2400	2025	525
Elongation at break (%)			
45	745	890	325
Forced vibrator at 100° C			
45			
Dynamic modulus, lb./sq. inch	89	111	218
Static modulus, lb./sq. inch	75	93	150
Internal friction, kilopoises	1.6	1.7	4.2
Young's bending modulus (° F for 10 ⁴ lb./sq. in.)			
45	-58	-56	-44

Reinforced Coral Compounds.—The similarity of Coral and natural rubber is also suggested by the properties of compounds reinforced with carbon black. Loaded with 35 parts of EPC black, a Coral compound had an internal friction* of 1.7 kilopoises, compared to 1.6 for natural rubber and 4.2 for LTP.

Coral rubber, like Hevea, is much superior to LTP in retention of properties at elevated temperatures (from 212° to 275° F) as shown in data (Table VII) from stocks compounded with 35 parts EPC black.

Low hysteresis and good retention of properties at elevated temperatures is

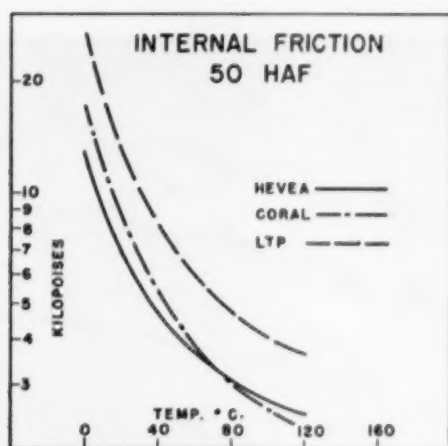


FIG. 4.—Internal friction as a function of temperature.

also apparent in Coral rubber stocks compounded with 50 parts HAF black (Figure 4 and Table VIII).

CORAL RUBBER IN TIRES

Coral rubber was used to build body plies, tread plies, inserts, and treads of size 9.00-20 truck tires. Hevea tread plies were used in the LTP tires. The Hevea tires contained all Hevea rubber. In this test both the Hevea and Coral tires were run simultaneously on duplicate indoor wheels, and the temperature of each tire was recorded on the same chart at the same time. The recorded temperature curve of the contained air of the Coral tire was superimposed on the curve from the Hevea tire, thus showing that both tires developed the same temperature. The two curves were identical throughout the run except for a short period at the beginning, when the temperature of the Coral tire was slightly lower. This was in accordance with what had been anticipated from the heat build-up characteristics of the respective stocks (Table IX).

Of outstanding significance in tire service tests, amounting to more than 500,000 tire miles, has been the improved tread cracking resistance of Coral treads over Hevea treads (Figure 5). A possible explanation of this perform-

TABLE VIII
CARBON BLACK-REINFORCED CORAL VULCANIZATES
(HAF black, 50 parts)

	Raw polymer		Internal friction (kp.)	Vulcanizate		
	Inherent viscosity	Gel (%)		Tensile strength (lb./sq. in.)		
				Room temp.	212° F	275° F
CPP-1350	10.5	1.8	2.5	3000	1500	—
CPP-1356	10.7	3.3	2.5	3550	1875	—
CPP-1462	11.6	4.5	2.6	3425	1900	1250
CPP-1416	14.9	7.0	2.9	3150	2025	—
CPP-1419	14.5	1.5	2.8	3375	1825	—



Coral—12,000 miles, no cracking
Hevea—12,000 miles, cracking
FIG. 5.—Improved tread crack resistance of Coral treads on 8.00-15 passenger car tires.

TABLE IX
VULCANIZATE PROPERTIES OF TIRE STOCKS

	Hevea	Coral polymers			LTP
		CPP-1415	CPP-1443	CPP-1550	
Inherent viscosity of raw polymer	—	16.0	13.0	18.9	—
Tread stocks (50 parts HAF black)					
Cure 60 min. at 280° F					
300% modulus (lb./sq. in.)	1900	1625	1275	1550	1650
Tensile strength (lb./sq. in.)	3675	3275	3100	3325	3575
Elongation (%)	500	540	480	560	520
Tensile strength (aged 2 days at 212° F) (lb./sq. in.)	1500	2675	2275	2600	2975
Internal friction (kp.)	2.5	2.9	2.6	2.4	4.5
Ring tensile strength (lb./sq. in.)					
At 212° F	2275	1600	1550	1850	850
At 275° F	1350	1150	850	1250	525
Cord ply stock (20 parts HAF black)					
	Hevea	Coral		LTP	
Cure 45 min. at 280° F.					
300% modulus (lb./sq. in.)	775	600		500	
Tensile strength (lb./sq. in.)	4100	3025		1475	
Elongation (%)	630	680		510	
Ring tensile strength at 212° F (lb./sq. in.)	1300	1150		225	
Internal friction (kp.)	0.6	0.55		1.36	

* Air oven.

ance may be associated with the lower oxygen absorption of Coral polymer. This may have some bearing on physical properties, since less oxygen absorption during breakdown or processing could influence the modulus, carbon black gel, and other characteristics (Figure 6).

To date, the best wear performance has been 95 per cent of that of natural rubber, determined on passenger tires under high-speed testing conditions in Texas. Although evidence of tread wear performance equivalent to that of natural-rubber treads was not a major objective in this work, it is thought that minor improvements in technology and polymer will result in equivalent wear.

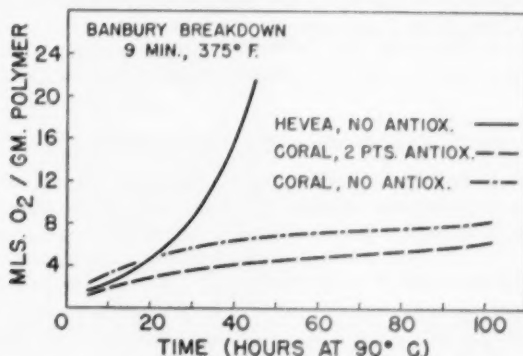


FIG. 6.—Oxygen absorption of Coral and Hevea rubber.

CONCLUSIONS

The data presented here support the contention that a polyisoprene rubber of high *cis*-1,4-content (Coral rubber) has been developed, which is strikingly similar in polymer structure to Hevea rubber, as indicated by infrared structure, x-ray crystalline pattern, perbenzoic acid determination of 1,4-addition, ozonolysis, unsaturation, carbon-hydrogen ratio, molecular-weight distribution, inherent viscosity, and specific gravity.

It is also shown that those polymer structural features and other characteristics of Coral rubber provide evidence that these same structural features found in natural rubber account for its low hysteresis, high gum tensile strength, and good retention of physical properties at elevated temperatures.

Coral rubber differs from Hevea rubber in that it has slightly less *cis*-1,4-structure and slightly more 3,4-structure; it does not absorb oxygen as readily as natural rubber, has higher thermal stability, and is more resistant to cracking in tire treads.

Both Hevea rubber and balata (both being polyisoprenes) have small amounts of 3,4-structure in the polymer chain rather than exclusively 1,4-structure as heretofore generally accepted.

In truck tires containing 100 per cent Coral rubber, the heat build-up during service (50 m.p.h.) was identical to tires built from natural rubber. Truck tires having Coral body stocks gave satisfactory performance in normal commercial service.

Tread wear road tests on truck and passenger tires show that Coral rubber treads, containing similar amounts and type of carbon black as Hevea treads, give 95 per cent of the wear obtained with Hevea treads.

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REFERENCES

- ¹ Prettyman, *Ind. Eng. Chem.* **34**, 1294 (1942); *RUBBER CHEM. AND TECHNOL.* **16**, 127 (1943).
- ² Wall, Brown, and Hart, *J. Polymer Sci.* **15**, 157 (1955).
- ³ Sands and Johnson, *Anal. Chem.* **19**, 261 (1947).
- ⁴ Hanson and Halverson, *J. Am. Chem. Soc.* **70**, 779 (1948); Arlman, *RUBBER CHEM. AND TECHNOL.* **23**, 306 (1950).
- ⁵ Kolthoff and Lee, *J. Polymer Sci.* **2**, 206 (1947).
- ⁶ Dillon, Prettyman and Hall, *J. Appl. Phys.* **15**, 309 (1944).

AMERIPOL SN—A CIS-1,4-POLISYOPRENE *

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INTRODUCTION

The important observation made by Katz¹ in 1925, using x-ray diffraction technique, showed that the mere stretching of crude or soft vulcanized Hevea rubber caused at least a portion of the polymer to undergo crystallization. This and the subsequent experiments of Hock² emphasized the point that successful attempts to synthesize a polymer resembling Hevea rubber would have to take regularity into account. The situation is complicated in isoprene polymers by the variety of ways the monomer can enter the growing polymer chain.

Four isomeric forms of polyisoprene are shown in Figure 1. Since head-to-tail orientations must be considered because of the asymmetry of the isoprene molecule, there are eight possible arrangements of the units that can occur in polymerized isoprene. Sodium, potassium, emulsion, and alfin polyisoprenes have been shown to contain all four forms of the repeating units³. All these uncured polymers have poor tack, and their pure-gum vulcanizates show poor physical properties. They do not crystallize when stretched or cooled. It has long been recognized that polymers of conjugated hydrocarbon dienes would have to be very regular in structure before their properties would approach those of Hevea rubber.

Looking back over the last fifteen to twenty years, there has been a slow development, almost imperceptible at first, of catalyst systems which produce polymers that in some degree show an oriented structure. This orientation could result if the monomer, during the propagation phase of the polymerization, is held in a definite position with respect to the growing chain, as by cybotactic forces where polymerization is initiated at the melting point of the monomer, or by adsorption of the monomer onto a solid surface—perhaps to the surface of the catalyst itself.

The work reported here deals primarily with the properties of a rubber made by directed polymerization.

POLYMER STRUCTURE AND PROPERTIES

Catalyst.—Catalyst systems, based on polyolefin information purchased from Karl Ziegler, have been applied to isoprene monomer systems, and modifications have been developed such that either *cis*-1,4-polyisoprene or *trans*-1,4-polyisoprene can now be prepared at will.

Infrared absorption spectra.—The effect of one of these catalyst modifications

* In this project, the different fields of activity of the eight authors were as follow: *Polymer structure and properties*—S. E. Horne, Jr., J. P. Kiehl, J. J. Shipman, V. L. Holt, and C. F. Gibbs. *Processing and vulcanization*—E. A. Willson and E. B. Newton. *Tire testing*—M. A. Reinhart and E. A. Willson. The paper is reprinted from *Industrial and Engineering Chemistry*, Vol. 48, No. 4, pages 784-791, April 1956, and was presented by F. K. Schoenfeld in behalf of Goodrich-Gulf Chemicals, Inc., before the Division of Rubber Chemistry of the American Chemical Society at its meeting in Philadelphia, November 2-4, 1955.

was first recognized when a modified olefin polymerization yielded an isolable unstabilized rubbery component which showed an infrared absorption spectrum (2- to 25-micron range) almost identical to that of Hevea rubber except for peaks due to oxidation at 2.8, 5.6, and 5.8 microns and, additionally, a slightly higher intensity in the peak at 11.25 microns. Subsequent samples of this rubber, a *cis*-1,4-polyisoprene, now called Ameripol SN, when protected by age resistors, did not show these oxidation peaks (Figure 2).

Infrared absorption spectra indicate low maximum concentrations of 1,2- and 3,4-addition products in Ameripol SN. For these two isomeric units the discrimination in the presence of *cis*-1,4-polyisoprene units is good, of the order ± 1 per cent. The discrimination of small amounts of *trans*-1,4-units in the presence of a large concentration of *cis*-1,4-units is not good, for, if we add by

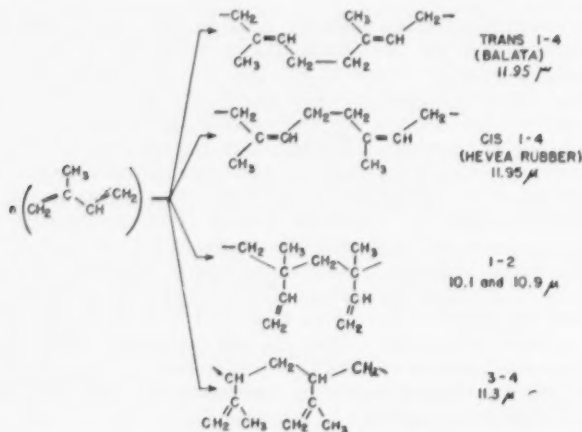


FIG. 1.—Four isomeric forms of polyisoprene and characteristic infrared absorption peaks.

common solvent technique 5 parts of balata to 100 parts of Hevea rubber, detection of the added balata is very difficult. In the region from 8.0 to 10.5 microns, where the spectrum of amorphous balata is most unlike that of Hevea rubber, the spectra of Hevea rubber-balata mixtures are practically superimposable on that of Hevea rubber alone. At least 10 parts of balata per 100 parts of Hevea rubber are required for detection (Figure 3). Single isolated *trans*-1,4-polyisoprene units would not necessarily have the same set of absorption bands as totally *trans*-1,4-polymer chains. At least four *trans*-1,4-units in a block are required to produce a spectrum resembling that of balata. These limitations of the infrared absorption technique apply to both synthetic and natural polyisoprenes.

Since it has been noted in this work as well as in the previous work of Richardson and Sacher³ and of Binder and Ransaw⁴ that infrared absorption techniques do not offer sufficient discrimination for accurately measuring the concentration of *trans*-1,4-isomer in predominately *cis*-1,4-samples of polyisoprene, we concluded that such a quantitative analysis for characterizing a material having less than 10 per cent *trans*-1,4-units was not feasible at this time. Instead, we estimated the maximum possible amounts of each isomeric impurity from the infrared spectra.

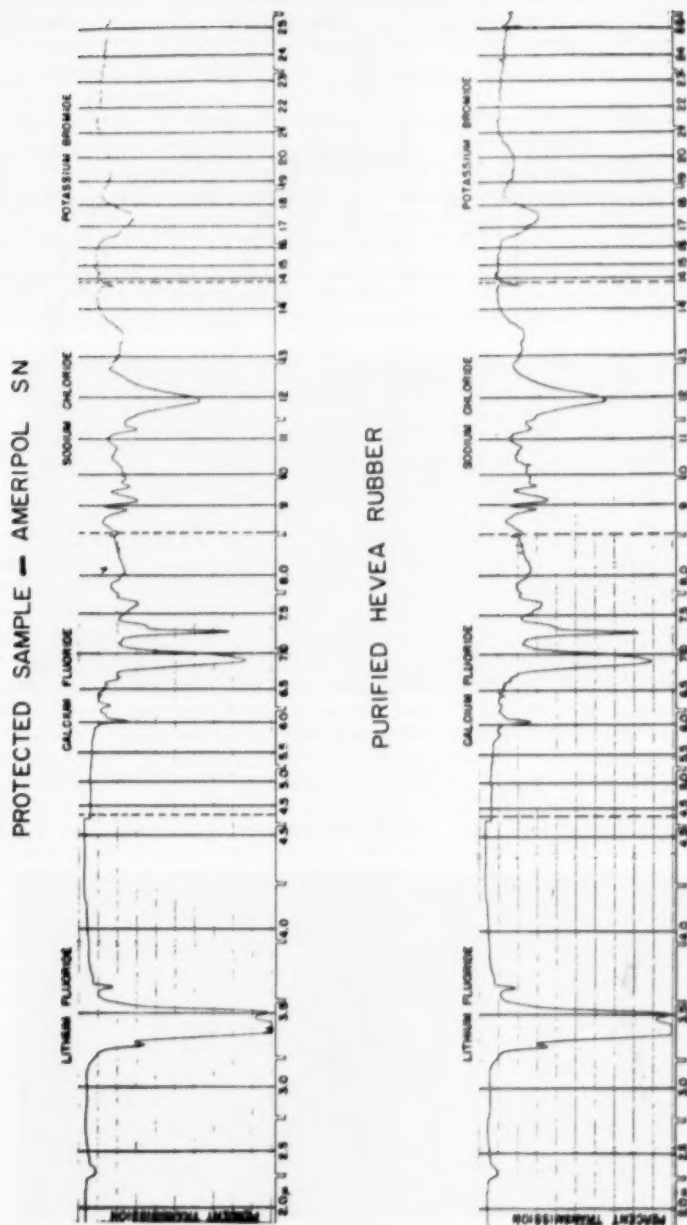


FIG. 2.—Comparison of the infrared spectra of Ameripol SN and Hevea rubbers. Films on potassium bromide disks.

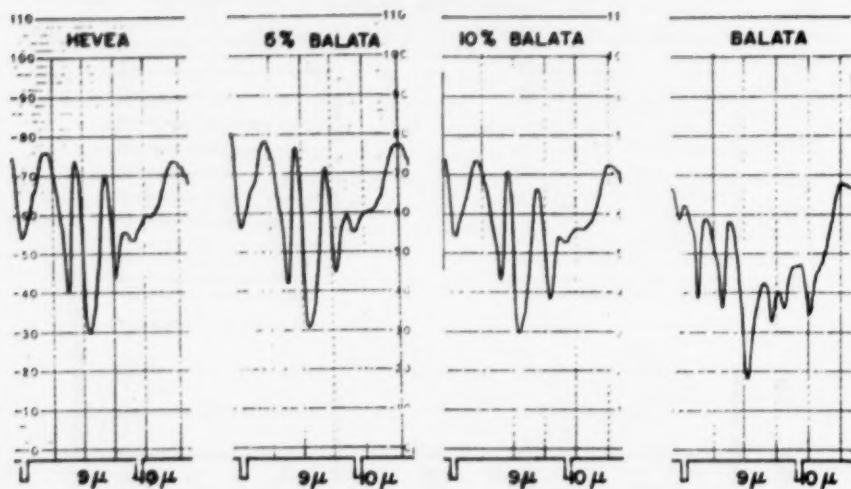


Fig. 3.—Infrared absorption spectra of Hevea rubber-refined balata mixtures.

The spectrum of Ameripol SN protected with an antioxidant duplicates that of the natural product except for the slight increase in intensity at 11.25 microns, which may be attributable to the presence of about 1 per cent more 3,4-addition product than is present in Hevea rubber. To the best of our knowledge, the origin of the 11.25-micron peak in the spectrum of Hevea rubber has not been established. Salomon and van der Schee⁵ say it is tempting to assign the 11.25- μ peak to 3,4-addition structure, but they found it survived ozonization.

The spectra of Ameripol SN and Hevea rubber in the region around 10.9 microns are very much the same, indicating very little difference in 1,2-addition product concentration. Thus the amount of side chains formed by 1,2-addition is estimated to be less than 1 per cent for both Hevea rubber and Ameripol SN.

It is not known what the differences in the infrared spectra of *cis*-1,4-head-to-tail polyisoprene and of *cis*-1,4-head-to-head polyisoprene would be like be-

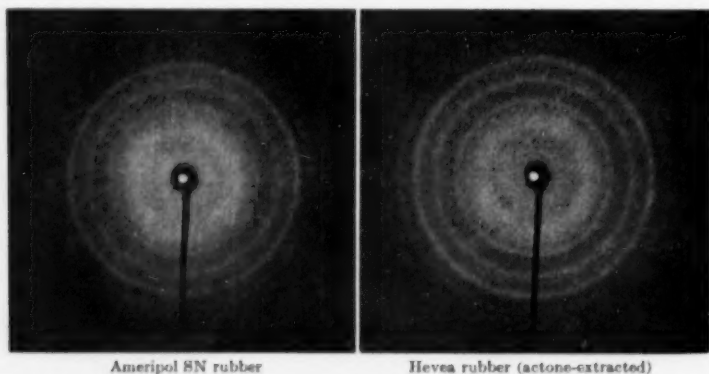


Fig. 4.—X-ray diffraction patterns of frozen but unstretched specimens.

cause polymers of the latter type are not available. It appears safe to assume that some of the skeletal vibrations would be affected, producing differences in the spectra. Since no differences except those already mentioned are apparent, it is reasonable to say that no great differences in head-to-tail orientation exist between Ameripol SN and Hevea rubber.

Examination by phase microscopy.—Crystalline and amorphous balata are insoluble in Hevea rubber and Ameripol SN. Concentrations as low as 2 per cent of balata in either of these polymers are detectable by phase microscopy in the mixtures. Since gel-free fractions of Ameripol SN and Hevea rubber hydrocarbon show a single phase by this method, we conclude that each contains less than 2 per cent of *trans*-1,4-polymer chains. This technique is applicable only if all the *trans*-1,4-units are in separate polymer chains. If the *trans*-1,4-units are distributed along predominately *cis*-1,4-polymer chains, insolubility would not result, and detection by this means would be impossible.

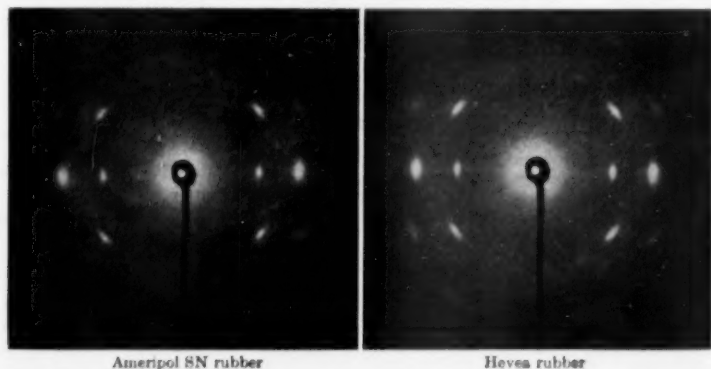


Fig. 5.—X-ray diffraction patterns of pure gum vulcanizates at 1000% elongation.

X-Ray diffraction patterns.—Ameripol SN crystallizes when cooled, as does Hevea rubber. The initiation period for Ameripol SN at -26°C is much longer than that for acetone-extracted Hevea. This is believed to be due to the absence of impurities which furnish nuclei for crystal growth. Seeding with stearic acid greatly reduces the initiation time. The rate of crystal growth in Ameripol SN at -26°C was slower than in the acetone-extracted Hevea rubber used. Crystallization rate is also affected by impurities. Figure 4 shows the x-ray diffraction patterns of unseeded Ameripol SN and of acetone-extracted pale crepe. The pale crepe was cooled at -26°C for 24 hours and held at this temperature during exposure. The Ameripol SN was cooled at -26°C for 140 hours and then photographed at this temperature. These ring diagrams are typical of nonoriented, finely divided crystals. The slightly mottled appearance of the rings is due to the Styrofoam frost shield used during the experiment. The ring diameters are the same in the two patterns, indicating identical crystal structures. The ratio of ring intensity to halo intensity is not quite the same in both patterns; degree of crystallinity is somewhat higher in the Hevea rubber sample. Hevea rubber shows its maximum rate of crystallization⁶ at -26°C ; hence this temperature was used for these experiments. It is not yet known whether Ameripol SN shows its maximum rate of crystallization at this same temperature.

Vulcanizates of Ameripol SN and Hevea rubber crystallize when stretched. Figure 5 shows the x-ray diffraction patterns of stretched vulcanizates at room temperature. The spot diagrams are essentially identical, indicating the same crystal structure and about the same degree of crystallinity in each case. The agreement here is as good as for two different samples of Hevea rubber. The fact that the two materials form crystals of identical structure precludes any large differences in head-to-tail orientation. It is impossible for head-to-tail oriented polymer of isoprene to form crystals of the same type and dimensions as a head-to-head polymer, even though the repeating units are otherwise identical.

From the infrared data, phase microscopy examination, and the x-ray diffraction data, we conclude that Ameripol SN and Hevea rubber are essentially similar in molecular structure and both contain less than 2 per cent predominantly *trans*-1,4-polymer and probably less than 10 per cent distributed *trans*-1,4-units. This concentration or higher of distributed *trans*-1,4-units in the polymers would be expected to seriously interfere with their ability to crystallize which, actually, neither polymer lacks.

TABLE I
POLYMER PROPERTIES OF AMERIPOL SN

$[\eta]_0$ = limiting intrinsic viscosity value M_n = number-average molecular weight M_v = viscosity-average molecular weight μ_1 = measure of degree of solvation of polymer molecules by solvent molecules							
Sample	Gel %	Swelling index	$[\eta]_0$	M_n	M_v	M_v/M_n	μ_1
Ameripol SN	6.3	126	3.80	230,000	658,600	2.86	0.398
Ameripol SN	0	—	1.32	77,200	135,000	1.75	0.406
Milled pale crepe	0	—	1.47	118,700	157,700	1.33	0.431
Unmilled pale crepe	11.6	127	8.30	838,000	2,126,000	2.54	0.434

Second-order transition temperature.—The second-order transition temperature (T_g) of a sample of Ameripol SN rubber was measured in a differential expansion apparatus similar to that described by Floyd⁷ and was found to be -70°C , which is the same as that obtained for smoked sheet and pale crepe in the same apparatus. The coefficients of expansion below and above the second-order transition temperatures agree also with published values within the 5 to 10 per cent reproducibility of the experiment.

The second-order transition temperature is roughly the temperature at which segmental motion of the polymer chain ceases. The balance between thermal disordering forces (moving the chain) and van der Waal (or intermolecular) forces is fairly critical to changes in polymer or copolymer composition. (A few per cent of most comonomer units will change the second-order transition temperature by several degrees.) Hence, the identity of T_g values is another indication of the identity of chain composition.

Polymer properties of Ameripol SN and Hevea rubber samples.—Using toluene as the solvent, sol-gel measurements were carried out at room temperature (in the dark), employing essentially the procedure recommended by the Office of Rubber Reserve, Committee on Standardization of Methods and Apparatus for Determining Molecular Weights of Polymers.

Intrinsic-viscosity measurements were made at $25.00^\circ \pm 0.01^\circ\text{C}$ over a

concentration range and were extrapolated to zero concentration to obtain the limiting intrinsic viscosity value which is designated by the symbol $[\eta]_0$. Cannon-Fenske type viscometers (50 Series) were employed for the viscosity determinations.

Using toluene solutions of the polymers, osmotic pressure measurements were made at $25.00^\circ \pm 0.01^\circ \text{C}$. Regenerated cellulose film was employed as the semipermeable membrane.

It is of interest to compare a few of the polymer properties of SN rubber with Hevea rubber. Some of the pertinent data relating to polymer properties such as gel content, swelling index, M_n (number-average molecular weight), M_v (viscosity-average molecular weight), $[\eta]_0$ and μ_1 values are summarized in Table I.

A sample of Hevea (pale crepe) was found to have a gel content of 11.6 per cent, with a swelling index of 137. The toluene-soluble portion yielded an

TABLE II
STABILIZATION OF AMERIPOL SN RUBBER, QUALITATIVE SCREENING TEST

Stabilizer	Parts/ 100 parts rubber	η_{sp} (0.5% in toluene)	
		Un- heated	Heated 8 hr. at 100° C
Diphenyl- <i>p</i> -phenylenediamine	0.25	3.39	2.51
2,5-Di- <i>tert</i> -butylhydroquinone (Santovar O)	0.2		
Bis(dimethylthiocarbamyl) disulfide (Tuada)	0.2	6.40	1.08
Mercaptobenzothiazole (Captax)	0.2	2.87	1.02
Bis(2-benzothiazyl) disulfide (Altax)	0.2	2.68	1.30
Sulfur	0.2	3.04	1.08
Polymerized trimethyldihydroquinoline (AgeRite Resin D)	1.0	3.27	1.20
1,2-Dihydro-2,2,4-trimethyl-6-phenylquinoline (85%)	1.0	3.04	1.84
Diphenyl- <i>p</i> -phenylenediamine 15% (Santoflex BX)			
<i>sym</i> -Di- β -naphthyl- <i>p</i> -phenylenediamine (AgeRite White)	0.5	3.43	2.34
Diphenyl- <i>p</i> -phenylenediamine	0.25		
<i>sym</i> -Di- β -naphthyl- <i>p</i> -phenylenediamine (AgeRite White)	0.5	2.60	1.92
2,5-Di- <i>tert</i> -butyl hydroquinone (Santovar O)	0.2		

$[\eta]_0$ value of 8.30 and an M_n value of 838,000. Using the equation of Carter, Scott, and Magat⁴ of $[\eta] = 5.02 \times 10^{-4} M^{0.467}$, an M_v value of 2,126,000 was calculated. The ratio of M_v/M_n was 2.54 which indicated a wide distribution of molecular weights.

A sample of moderately high molecular weight Ameripol SN rubber contained 6.3 per cent gel with a swelling index of 126. The toluene-soluble component had an $[\eta]_0$ value of 3.80. The high swelling index value of 126 encountered for a gel content of 6 per cent was similar to sol-gel data obtained for some natural rubber samples. This type of a gel structure is easily broken down by normal milling and processing operations. M_n and M_v values of 230,000 and 658,600 were obtained for this SN rubber. The ratio of M_v/M_n was 2.86 which suggests a wide distribution of molecular weights similar to that indicated for the unmilled pale crepe rubber.

Hevea (pale crepe) rubber was milled on a cold mill for 20 minutes. It was totally soluble in toluene. The $[\eta]_0$, M_v , and M_n values were, respectively,

1.47, 157,700, and 118,700. This gave a ratio of 1.33 for M_w/M_n . Cold milling of the Hevea rubber resulted in a polymer with a narrower distribution of molecular weights compared to the original pale crepe rubber.

A low molecular weight Ameripol SN rubber was found to be totally soluble in toluene. The $[\eta]$, M_w , and M_n values were, respectively, 1.32, 135,000, and 77,200. The ratio of 1.75 for M_w/M_n indicated a broader distribution of molecular weights than in the milled pale crepe rubber.

A comparison of the μ_1 values of the rubber-toluene systems is of interest. The μ_1 value is a measure of the degree of solvation of polymer molecules by solvent molecules. For the binary system of natural rubber-toluene at 27° C, a μ_1 value of 0.43 was reported by Huggins⁹.

TABLE III
STABILIZATION OF AMERIPOL SN RUBBER
OXYGEN ABSORPTION AT 100° C

		r_0 = initial rate of oxidation (mole O_2 /gram ⁻¹ min. ⁻¹)	k = measure of autocatalytic nature of oxidation (min. ⁻¹)
Polymer	Stabilizer	r_0	k
Ameripol SN	None	5.0×10^{-7}	96×10^{-4}
Ameripol SN	2,5-Di- <i>tert</i> -butyl hydroquinone (Santovar O), 0.5% on rubber	0.25×10^{-7}	6.3×10^{-4}
Ameripol SN	Diphenyl- <i>p</i> -phenylenediamine, 0.2% on rubber	0.40×10^{-7}	21×10^{-4}
Ameripol SN	<i>sym</i> -Di- β -naphthyl- <i>p</i> -phenylenediamine (Age-Rite White), 0.5% on rubber	0.10×10^{-7}	0.64×10^{-4}
Ameripol SN	<i>sym</i> -Di- β -naphthyl- <i>p</i> -phenylenediamine (Age-Rite White), 0.5% on rubber	0.10×10^{-7}	~ 0
	2,5-Di- <i>tert</i> -butyl hydroquinone (Santovar O), 0.2% on rubber		
Hevea pale crepe	None added	0.19×10^{-7}	2.2×10^{-4}

The high and the low molecular weight Ameripol SN rubber samples yielded μ_1 values of 0.406 and 0.398 at 25.00° C. Unmilled pale crepe and milled pale crepe had μ_1 values of 0.434 and 0.431, respectively, at 25.00° C; this represents a good check on the value of 0.43 reported by Huggins.

At the present time it is believed that the difference between the μ_1 values of Ameripol SN and Hevea rubber is real. These data imply that the Hevea rubber molecules are less solvated by toluene than are the Ameripol SN rubber molecules. This may be due to the presence of a more highly branched structure in the Hevea molecule compared to the SN molecule, or it may be a reflection of the presence of a small amount of nonrubber components in the Hevea samples.

Solvents having solubility parameter values of 8.6 ± 1.35 appeared to be good solvents for both Ameripol SN rubber and milled pale crepe rubber. Carbon tetrachloride was the best solvating agent for both materials. Other good solvents were chloroform, cyclohexane, carbon disulfide, chlorobenzene, toluene, and benzene.

Stabilization of Ameripol SN.—Freshly made polymer must be stabilized to protect it from degradation and softening by atmospheric oxidation. Illustra-

tive of some of the early results of screening tests are the examples in Table II. Aliquots of a polymer charge were mill mixed (eight passes) with the materials shown and exposed as 0.015-inch-thick sheets both at room temperature (unheated) and (heated) in a circulating air oven for 8 hours at 100°C; specific viscosities (at 0.5 per cent concentration in toluene) were then determined. As one would expect, some materials and combinations were more effective than others in stabilizing the raw polymer. The effectiveness of the stabilization of some of these Ameripol SN rubber samples prepared by the addition of the more promising commercial stabilizers or antioxidants was further determined by measurements of the rate at which various polymer samples reacted with oxygen at elevated temperatures. An apparatus that made possible

TABLE IV
PHYSICAL PROPERTIES OF VULCANIZATES—GUM STOCK
(Room temperature tests)

Cure (min. at 280° F)	Ameripol SN		Hevea rubber			
	No addi- tive	Plus 1.5 parts of additive*	Tech. classified grades			Test blend
			Red O	Yellow O	Blue O	
			Tensile strength (lb./sq. inch)			
15	No cure	2840	800	2540	2900	2490
30	1400	3550	2680	3150	3970	3410
45	2030	3440	2970	3850	3810	3210
60	2380	3200	3090	3450	4000	3670
90	2250	3210	3110	3600	3730	3620
600% Modulus (lb./sq. inch)						
15	—	350	260	380	500	380
30	120	700	550	790	970	790
45	280	800	700	1110	1200	950
60	350	800	930	1280	1320	1170
90	430	700	1040	1400	1520	1240
Elongation at break (%)						
15	—	930	870	890	860	910
30	990	850	820	800	830	830
45	910	880	790	780	760	790
60	860	750	760	750	770	760
90	800	820	750	700	750	760

*Lecithin (95%) and TEA (5%).

ACS II Recipe: Rubber 100, zinc oxide 6, stearic acid 4, Captax 0.5, sulfur 3.5; ACS tensile sheet.

measurements of the volume of oxygen consumed at constant pressure and temperature was employed. All measurements were made at a temperature of $100^{\circ} \pm 0.2^{\circ} \text{C}$ and at approximately 760 mm. of mercury pressure.

The curves of oxygen consumed versus time were all of an autocatalytic nature, oxidation rate increasing with time. Two parameters can be obtained from such curves: The first is the initial rate of oxidation, designated r_0 , and the second is a factor designated by k which is a measure of the autocatalytic nature or self-acceleration of the oxidation. Table III shows typical data from a series of oxidation rate measurements. Decreased values of r_0 , of course, correspond to more efficient stabilization, as do decreased values of k . For this series, AgeRite White is the most efficient stabilizer, Santovar O being next. Both AgeRite White and the combination of AgeRite White and Santovar O shown have stabilized the Ameripol SN to a degree equivalent to or better than that

shown by pale crepe. The unstabilized Ameripol SN polymer is very susceptible to oxidation at 100° C.

The addition of stabilizers decreased the initial rate of oxidation by a factor of approximately 20, whereas k was decreased by a factor of almost 100.

PROCESSING AND VULCANIZATION

Ameripol SN, as ordinarily made, looks and handles much like masticated Hevea rubber. It has excellent tack and good "tooth". The Mooney viscosity (ML-4' at 212° F) of the polymer is in the 50 to 75 range.

TABLE V
PHYSICAL PROPERTIES OF VULCANIZATES—
LOW-SULFUR GUM COMPOUND
(Room temperature tests)

Cure (min. at 260° F)	Ameripol SN*	Hevea Rubber*
	Tensile strength (lb./sq. inch)	
10	2420	No cure
20	2900	2880
30	3180	3280
40	3100	3300
	600% Modulus (lb./sq. inch)	
10	200	—
20	420	420
30	400	500
40	400	350
	800% Modulus (lb./sq. inch)	
10	1100	—
20	1900	1720
30	2200	1900
40	2000	1550
	Elongation at break (%)	
10	930	—
20	860	920
30	830	900
40	860	980

Recipe: Rubber 100, zinc oxide 1, AgeRite White 0.5, fat acid activator 2.5, Captax 0.4, Altax 0.55 sulfur 1.5; ACS tensile sheets.

* Additives: 1 part stearic acid; 1.5 parts lecithin plus TEA

* Additive: 1 part rosin oil.

Processing properties.—Ameripol SN requires no preliminary breakdown and bands smoothly on a laboratory mill by the time the rolls have made three or four revolutions. This is partly due to the excellent natural tack of the polymer. Like natural rubber, Ameripol SN breaks down rapidly on a cold mill, so mill mixing is usually carried out at temperatures around 180° F. Compounding ingredients then added are accepted as readily and dispersed as well as they would be in Hevea rubber.

Laboratory Banbury mixing is usually run at 220° to 260° F, in which range the stocks handle well, but batches have been discharged satisfactorily at 325° F. Factory Banbury mixing presented no problem, and Ameripol SN stocks processed well on factory calenders and in extruders. In fact, extruded treads showed less linear shrinkage and less extrusion porosity than ordinary Hevea rubber treads. The carcass plies and the treads handled well in the factory

tire-building operation, and the building tack of the Ameripol SN was equivalent to that of similar Hevea rubber stocks.

Compounding.—Freshly made Ameripol SN lacks three kinds of materials (naturally present in Hevea rubber) that are known to have an important

TABLE VI
PHYSICAL PROPERTIES OF VULCANIZATES—CARCASS STOCKS

	Ameripol SN		Hevea rubber
	I	II	
Gel (%)	14	31	—
Swelling index	83	59	—
$[\eta]$	3.17	3.45	—
Mooney viscosity (ML-4' at 212° F)	75	75	—
Carcass recipe (parts)			
Polymer	100.0	100.0	100.0
Zinc oxide	3.0	3.0	3.0
Stearic acid	2.0	2.0	1.0
AgeRite Powder (PBNA)	1.0	1.0	1.0
HMF black (Statex 93)	40.0	40.0	40.0
Pine tar	5.0	5.0	7.0
Lecithin + TEA (5%)	1.5	1.5	—
Altax	1.0	1.0	1.0
Sulfur	2.5	2.5	2.5
B. F. Goodrich plasticity, 85° C (on compounded stock)	72.8	66.4	72.8
Mooney scorch (260° F, large rotor)			
I.V., initial viscosity	36	42	34
V_m , min. viscosity	26	32	25
T_s , scorch time (min.)	20.9	17.3	16.9
$T_s(T_s + T_{\Delta 20})$, cure time (min.)	27.6	21.3	20.5
$T_{\Delta 20}$, min. for 20-point viscosity increase	6.7	4.0	3.6
Gehman low-temperature modulus (cure 30 min., 280° F) (° C)			
T_2	-33	-32	-34
T_3	-48	-48	-49
Freeze point	-58	-58	-59

Stress-strain at room temperature

Cure (min. at 280° F)	Tensile strength (lb./sq. in.)		
	I	II	Hevea rubber
10	150	680	1820
15	1070	2260	2930
30	2840	2880	3580
60	2910	2650	3240
150	2420	1500	2720
	400% Modulus (lb./sq. in.)		
	I	II	Hevea rubber
10	—	200	630
15	360	780	1650
30	880	1260	1370
60	1080	1300	1340
150	1040	1160	1220
	Elongation at break (%)		
	I	II	Hevea rubber
10	940	660	640
15	720	690	690
30	710	630	670
60	670	610	640
150	650	470	610

Ameripol SN
I III Hevea rubber

TABLE VI—(Continued)

Stress strain at 212° F

Cure (min. at 280° F)	Tensile strength (lb./sq. in.)		
10	—	230	1200
15	900	1650	2180
30	1620	1500	2290
60	1330	1300	1920
150	1320	1220	1820
	400% Modulus (lb./sq. in.)		
10	—	—	220
15	150	400	520
30	560	740	830
60	700	800	750
150	700	780	660
	Elongation at break (%)		
10	—	1000	940
15	1040	800	900
30	850	660	790
60	700	610	760
150	700	600	800

Aged in test-tubes 24 hours at 212° F in air; Stress-strain at room temperature

Cure (min. at 280° F)	Tensile strength (lb./sq. in.)		
10	1770	2500	2680
15	2220	2800	3140
30	2450	2540	3080
60	1880	2230	2780
150	2030	2100	2380
	400% Modulus (lb./sq. in.)		
10	700	1000	1800
15	800	1200	1840
30	1050	1440	1650
60	1280	1620	1480
150	1080	1320	1120
	Elongation at break (%)		
10	650	650	510
15	680	640	590
30	640	560	600
60	520	500	600
150	600	570	620

Graves angle tear (212° F)

Cure (min. at 280° F)	lb./in.		
15	60	130	180
30	210	190	220
60	190	170	220

B. F. Goodrich Flexometer (212° F); 55-lb. load; 60-min. cure (280° F)

Stroke, 0.175 inch			
Shore A hardness	48	52	49
ΔT (° F)	27	25	25
Permanent set (%)	10.4	6.7	7.5
Static compression at 55 lb. (%)	28.8	24.3	27.3
Duration of test (min.)	25	25	25
Stroke, 0.225 inch			
Shore A hardness	47	52	48
ΔT (° F)	52	41	45
Permanent set (%)	15.3	8.5	10.5
Static compression at 55 lb. (%)	30.1	24.7	29.3
Duration of test (min.)	25	25	25

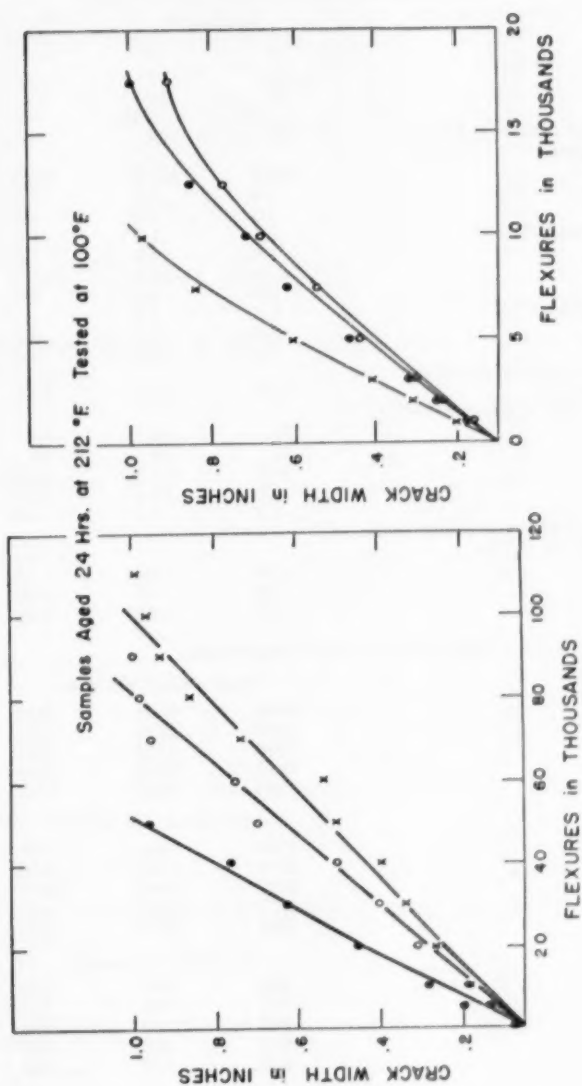


TABLE VII
 PHYSICAL PROPERTIES OF VULCANIZATES—TREAD STOCK

	Ameripol SN		Hevea rubber
	I	II	
Gel (%)	14	31	—
Swelling index	83	59	—
$[\eta]$	3.17	3.45	—
Mooney viscosity (ML-4' at 212° F)	75	75	—
Tread recipe (parts)			
Polymer	100.0	100.0	100.0
Zinc oxide	3.0	3.0	3.0
Stearic acid	4.0	4.0	3.0
AgeRite Powder (PBNA)	1.0	1.0	1.0
BLE-25	1.0	1.0	1.0
ISAF black	42.0	42.0	42.0
Pine tar	2.0	2.0	4.0
Lecithin + TEA (5%)	1.5	1.5	—
Santocure	0.6	0.6	0.6
Sulfur	3.0	3.0	3.0
B. F. Goodrich plasticity, 85° C (on compounded stock)	44.8	38.4	50.3
Mooney scorch, 260° F (large rotor)			
I.V.*	52	56	56
V_m	35	40	36
T_s	12.8	11.3	12.25
T_c	15.0	13.4	13.8
$T_{\Delta_{90}}$	2.2	2.1	1.55
Gehman low-temperature modulus (cure 30 min., 280° F) (° C)			
T_1	-33	-32	-34
T_2	-48	-48	-49
Freeze point	-58	-58	-59

Stress-strain at room temperature

Cure (min. at 280° F)	Tensile strength (lb./sq. in.)		
	I	II	Hevea
15	3810	3820	4040
30	4160	3810	4230
45	3900	3730	4080
75	3840	3700	3920
150	3540	3150	3490
	400% Modulus (lb./sq. in.)		
	I	II	Hevea
15	1580	1890	2110
30	2010	2300	2550
45	2250	2460	2570
75	2170	2360	2450
150	1900	2010	2200
	Elongation at break (%)		
	I	II	Hevea
15	690	640	630
30	650	580	570
45	600	550	570
75	600	560	580
150	630	570	560

Stress-strain at 212° F

Cure (min. at 280° F)	Tensile strength (lb./sq. in.)		
	I	II	Hevea
15	2700	2480	2860
30	2450	2100	2480
45	2220	2120	2490
75	2210	2000	2480
150	2170	1830	2400

TABLE VII—(Continued)

Stress-strain at 212° F

Cure (min. at 280° F)	400% Modulus (lb./sq. in.)		
	I	II	Hevea rubber
15	880	1120	1140
30	1150	1370	1290
45	1300	1500	1420
75	1290	1380	1500
150	1150	1280	1220
Elongation at break (%)			
15	840	690	770
30	700	580	600
45	620	570	600
75	600	520	600
150	600	520	650

Aged in test-tubes 24 hours at 212° F in air; Stress-strain at room temperature

Cure (min. at 280° F)	Tensile strength (lb./sq. in.)		
	I	II	Hevea rubber
15	3120	2990	2950
30	2890	2710	2810
45	2620	2570	2510
75	2120	2110	1880
150	1430	1360	1550
400% Modulus (lb./sq. in.)			
15	1900	2780	2640
30	2100	2400	2660
45	2340	2570	—
75	—	—	—
150	—	—	—
Elongation at break (%)			
15	600	530	450
30	550	470	440
45	450	400	380
75	380	330	300
150	280	270	290

Graves angle tear (212° F)

Cure (min. at 280° F)	Lb./in.		
15	270	250	340
30	270	240	360
45	280	240	300

B. F. Goodrich Flexometer (212° F); 55-lb. load; 60-min. cure (280° F)

Stroke, 0.175 inch			
Shore A hardness	62	64	61
ΔT (° F)	33	36	33
Permanent set (%)	10.8	10.3	9.4
Static compression at 55 lb. (%)	19.2	17.9	20.1
Duration of test (min.)	25	25	25
Stroke, 0.225 inch			
Shore A hardness	61	63	62
ΔT (° F)	83	74	68
Permanent set (%)	20.0	18.2	16.7
Static compression at 55 lb. (%)	20.4	19.1	21.3
Duration of test (min.)	25	25	25
Pico abrasion (B. F. Goodrich Research Center, unpublished method)	95	92	100

* See Table VI for definitions.

influence on the technical quality of vulcanizates—antioxidant for polymer stabilization, nonrubber components (such as ash, protein, and protein decomposition products), and fat acid material which affect the state of vulcanization. These deficiencies are corrected by additions of suitable materials. The antioxidant is added at once to every lot of the freshly made polymer accordingly as a nonstaining or staining type polymer is required. Addition of fat acid and a material simulating the nonrubber components is made by the compounder as required. Some buffer material¹⁰ is needed to help adjust the rate of cure of Ameripol SN, and in the tests reported the additive soybean lecithin (95 per cent) with triethanolamine (TEA) (5 per cent), was used (1½ parts of this mixture to 100 parts by weight of polymer). Otherwise, Ameripol SN is compounded and handled like Hevea rubber.

Pure-gum stocks.—Ameripol SN with additive shows good properties in the ACS-II test recipe (Table IV), approximating those shown by the Hevea rubber test blend of ribbed smoked sheet and pale crepe. In a low sulfur, pure-gum recipe (Table V), Ameripol SN containing both additive and extra fat acid gives a vulcanizate quite comparable to that of the Hevea rubber control.

Heavy-duty tire stocks.—It was a natural anticipation that this new polymer, Ameripol SN, so much like Hevea rubber in chemical structure, milling, compounding, and vulcanizing characteristics, should show low hysteresis values, as well, in heavy-duty truck tire stocks. Extended tests have amply borne this out.

Two different lots of Ameripol SN, labeled I and II, differing somewhat in gel content and in swelling index of the gel (determined on the unmilled polymer) were compounded in a typical carcass stock and in a tread stock along with a Hevea rubber test blend (ribbed smoked sheet and pale crepe) as a control. The recipes in each case are identical except for the lecithin-triethanolamine additive (1.5 parts/100 parts of Ameripol SN) and extra stearic acid (1 part/100 parts Ameripol SN) to approximate the amount naturally present in Hevea rubber. Comparative data on physical properties of the carcass stocks are shown in Table VI and in Figure 6; those on the tread stocks are shown in Table VII and in Figure 7. The stress-strain properties at room temperature, at 212° F, and after aging are very similar on all the stocks, as are the Gehman low temperature moduli and freeze points. The heat rise in the B. F. Goodrich flexometer at both 0.175- and 0.225-inch strokes are likewise comparable. The Graves angle tear tests at 212° F are somewhat lower than those for the Hevea stocks, but, on the other hand, the Ameripol SN stocks in the DeMattia flex crack-growth (initiated) tests appear on the whole to be more resistant than do those of the Hevea stocks.

Summary.—The results of the laboratory comparative evaluation tests on pure-gum carcass and tread stocks indicate a virtual identity in the performance of Ameripol SN rubber and Hevea rubber. The comparative data suggest that Ameripol SN heavy-duty tires will perform as well as similar Hevea rubber tires.

TIRE TESTING

The possibility of using Ameripol SN rubber to replace Hevea rubber completely in the tread and carcass stocks of heavy-duty bus and truck tires has undergone extensive testing. The results reported here deal with a lot of sixteen 11.00 × 20 heavy-duty express tires which required about 1 ton of Ameripol SN for manufacture.

The procedure for evaluation of test tires is divided into three programs, namely, indoor wheel tests, where tires are run to destruction; test truck opera-

tion, where conditions such as speed, load, and inflation are closely regulated; and mileage contract busses, where tire maintenance is at a high level, but service conditions on the highways are very severe.

Indoor wheel test.—Tires are run on smooth 67-inch-diameter wheels in an ambient temperature of $100^{\circ} \pm 5^{\circ}$ F at a speed of 50 miles per hour. This is a continuous 24-hour-per-day test, with the load increased in increments amounting to 20 per cent of the rated load capacity each 24 hours. The test is started at 80 per cent of standard Tire and Rim Association load. This is a very severe accelerated test and usually is terminated by a carcass blowout due to heat

TABLE VIII
INDOOR WHEEL TESTS
(Tests run according to old [prior to April 15, 1955 revision] Tire and Rim Association load ratings)

Test Miles	Load		Inflation pressure (lb./sq. in.)	Tire temp. ($^{\circ}$ F)	
	On tire (lb.)	% of standard		Crown	shoulder
Ameripol SN tire No. 1					
0	3600	80	70	—	—
0-1200	3600	80	85	210	187
1200-2400	4500	100	88	220	233
2400-3600	5400	120	89	235	249
3600-3675	6300	140	Tire failed at 3675 miles due to separation from carcass cord		
Ameripol SN tire No. 2					
0	3600	80	70	—	—
0-1200	3600	80	83	204	186
1200-2400	4500	100	86	216	205
2400-3600	5400	120	85	233	261
3600-3788	6300	140	Tire failed at 3788 miles due to heat blowout		
Hevea rubber tire No. 1					
0	3600	80	70	—	—
0-1200	3600	80	81	202	192
1200-2400	4500	100	80	220	246
2400-3600	5400	120	92	230	262
3600-3656	6300	140	Tire failed at 3656 miles due to heat blowout		
Hevea rubber tire No. 2					
0	3600	80	70	—	—
0-1200	3600	80	91	213	223
1200-2400	4500	100	90	218	240
2400-3600	5400	120	91	236	272
3600-4051	6300	140	Tire failed at 4051 miles due to heat blowout		

build-up. Hysteresis of compounds used is a strong influential factor of the mileage obtained to failure. The heat build-up in Ameripol SN rubber tires, measured by thermocouple needle and air pressure build-up in the tire, was slightly less than that in the Hevea rubber control tires. Tires evaluated by this method are always run to destruction. The mileages run by the Ameripol SN tires to failure were comparable to those shown by the Hevea rubber controls (Table VIII). Resistance to cut growth (standardized cuts are made in the tread grooves before the test is started) was somewhat better in the Ameripol SN tires (an average of 12 per cent increase of cut growth) than in the Hevea rubber control tires (an average of 26 per cent increase in cut growth).

Test truck operation.—This is also an accelerated service test, but of less

severity than the indoor wheel test. The test trucks are operated in the Kerrville, Tex., area, on a 24-hour-per-day basis at 45 miles per hour. Tires are rotated to the four wheel positions at 700 mile intervals. Test conditions such as loads, speeds, and inflation pressures are closely regulated. The test is operated at standard Tire and Rim Association load for 2800 miles, followed by 2800 miles at 130 per cent rated load, and then run to failure or completion of 19,600 miles (whichever occurs first) at 150 per cent rated load.

The Ameripol SN rubber tires made a very creditable showing. Tread wear was 85 per cent that of the standard Hevea control tires. (These particular Ameripol SN rubber treads were rerun several times through the tube machine during efforts to obtain proper die distribution. This had a deleterious effect on the abrasion quality of the treads.)

Resistance to growth of initiated tread cuts was good—comparable to controls. Independent cracking was inferior to the control (Table IX).

TABLE IX
TEXAS ROAD TEST
Conditions of test

Speed: 45 miles per hour

Tire size: 11.00 X 20 rayon construction

Test miles	Load on tire (lb.)	% of standard load rating	Inflation pressure (lb./sq. in.)
0-2,800	5150	100	75*
2,800-5,600	6700	130	75
5,600-19,600	7730	150	75

Tires made of	Results		Tread wear index
	Inches of cracking (independent) Total length	Initiated cracks (% growth)	
Ameripol SN No. 1	64	245	85
Ameripol SN No. 2	98	265	
Hevea rubber No. 3	20½	248	100
Hevea rubber No. 4	22½	191	

* Standard.

The carcasses of all the tires were sound after 19,600 miles of operation and have been recapped (a standard procedure) and placed in intracity bus operation service.

Mileage contract bus operation.—Tires have been placed in most rigorous intercity bus operational service. Speeds may be higher than 70 miles per hour. Loads naturally vary. The front wheel positions are usually overloaded (say, up to 130 per cent), while rear wheel positions are reasonably close to rated loads. It is customary to apply new tires to the front-wheel position, operate them for 15,000 to 25,000 miles, and then change tires to rear wheels. Such a routine is followed to obtain optimum service from the tires and to conform to the highest safety standards.

Ameripol SN rubber tires are operating very satisfactorily. The mileage on the individual tires naturally varies because they are running on different vehicles, but a particular lot of ten tires placed in intercity high speed bus service are all sound after accumulation of 600,000 miles of travel to the time of regrooving of the treads. Indications are that the tread wear index of Ameripol

SN tires is about 85 per cent that of the Hevea control tires. Independent tread cracking is inferior to that shown by the control tires, but the severity is not alarming. These service tests were initiated during the hot summer months, thus adding to the significance of the results obtained.

Summary.—From a practical standpoint, Ameripol SN is equivalent in properties to Hevea rubber. This new development has solved the long-standing problem of producing by synthetic means a general-purpose polymer adequate as a complete replacement for Hevea rubber in heavy-duty tires.

ACKNOWLEDGMENTS

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REFERENCES

- ¹ Katz, *Chem.-Zig.* **49**, 353 (1925).
- ² Hock, *Z. Electrochem.* **31**, 404 (1925).
- ³ Richardson and Sacher, *J. Polymer Sci.* **14**, 353 (1953).
- ⁴ Binder and Ransaw, Firestone Tire & Rubber Co., Rept. CR-3756 to Federal Facilities Corp., Office of Synthetic Rubber, Research and Development Division, Polymer Science Branch, Washington, D. C., April 22, 1955.
- ⁵ Salomon and van der Schee, *J. Polymer Sci.* **14**, 185 (1954).
- ⁶ Wood and Bekkedahl, *J. Appl. Phys.* **17**, 362 (1946).
- ⁷ Floyd, *Brit. J. Appl. Phys.* **3**, 373 (1952).
- ⁸ Carter, Scott, and Magat, *J. Am. Chem. Soc.* **68**, 1480 (1946).
- ⁹ Huggins, *Ann. N. Y. Acad. Sci.* **44**, 431 (1943).
- ¹⁰ Newton, *Ind. Eng. Chem.* **34**, 374 (1942).

POLYMER-MODIFIED NATURAL RUBBER *

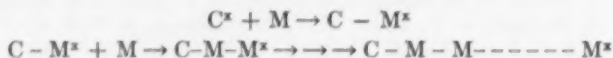
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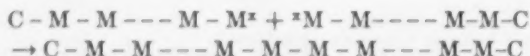
PRODUCTION AND CHARACTERIZATION OF GRAFT POLYMERS

INTRODUCTION

Polymerization of a monomeric compound such as methyl methacrylate to its polymeric form, i.e., to "Perspex," occurs according to a mechanism whereby the catalyst (C^*) first activates a monomer unit (M), which then combines with successive monomer units to build up a very long chain:

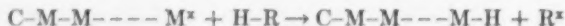


This continues growing until terminated by mutual combination with a similar growing chain:



giving a stable polymer molecule which in this case is glasslike and rigid.

Termination can occur by other means. Thus if a solvent (RH) containing a labile hydrogen atom is added to the system, some of the growing polymer chains may be terminated by the transfer of a hydrogen atom to give dead polymer, i.e.:



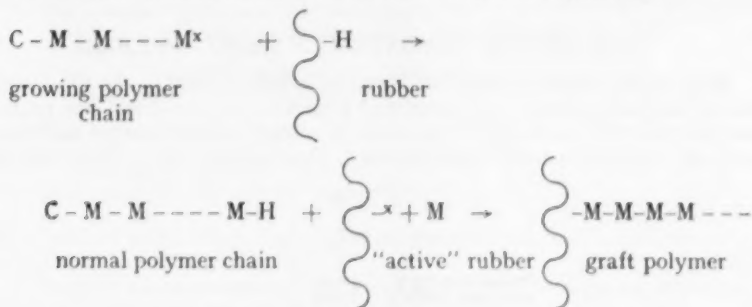
A new radical or active center R^* is formed, which reinitiates polymerization. This second polymer chain grows until it is either terminated again in a similar manner or by mutual combination as in the first instance. This sequence of reactions is known as transfer¹ and has important practical applications. Thus it is used, for example, in synthetic rubber production to control the length of the polymer chains formed.

The easier the reaction between the growing chain and RH, the shorter will be the final length of the polymer chains formed. This, therefore, affords a means of comparing the activity of different monomers towards substances containing labile hydrogen-atoms, among which is rubber and its homologs. We have done this for a solvent which should act chemically as a model for rubber, and the results indicate that the common monomers styrene, methyl methacrylate, methyl acrylate, and vinyl acetate increase in activity in that order².

* Reprinted from the *Proceedings of the Institution of the Rubber Industry*, Vol. 3, No. 1, pages 27-39, February 1956. The present address of F. M. Merrett is Fisons Ltd., Felixstowe, Suffolk, England; that of R. I. Wood is Cabot Carbon Co., Stanlow, Ellesmere, Cheshire, England.

APPLICATION TO RUBBER

In the case of simple transfer given above, the polymer chains initiated by the catalyst and RH (the transfer agent) are essentially the same from a polymeric point of view. If RH is rubber, then the chain terminated by the transfer of a hydrogen atom from the rubber will be a normal polymer molecule, but the chain subsequently formed will be attached to the rubber, i.e.:



Such graft polymers form one of the four main types shown in Figure 1. Rubber and methyl methacrylate themselves are simple polymers and synthetic rubber is a typical random copolymer. The graft and block copolymers consist essentially of long sequences of like units and hence can be made from preformed polymers. Graft polymers in particular were chosen because the above method seemed to afford a reasonable way of making them and their structure was such as to retain the good properties of the long chains of natural rubber while effecting sufficient modification to provide alternative or improved usage. For example, it was hoped to produce modulus reinforcement with good fatigue

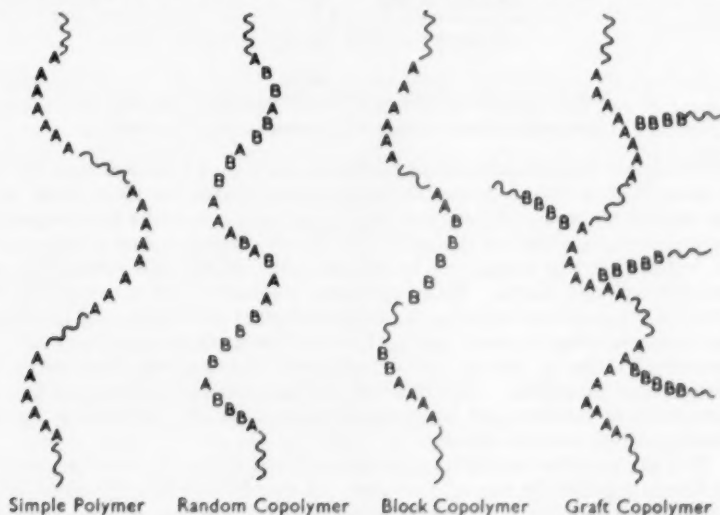


Fig. 1.—Principal types of polymers.

resistance. Variation in polar character or physical characteristics of the modifying polymer would also be relatively easy.

The aim of the first part of our program was to obtain proof of the formation of such graft polymers and to isolate them³. It was then proposed to characterize them as completely as possible, that is, to determine the number and length of the side chains added, as well as any alteration of the length or character of the rubber backbone.

METHODS FOR SEPARATION OF GRAFT POLYMERS

When methyl methacrylate, for example, is polymerized in the presence of rubber, the total product may consist of a mixture of unmodified free rubber, graft polymer (i.e., a chemical compound of rubber and polymethyl methacrylate), and free polymethyl methacrylate. This mixture can be separated by

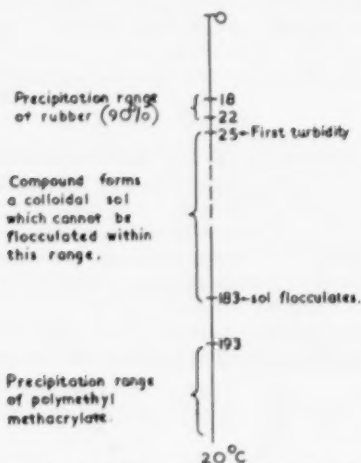


Fig. 2.—Separation method for rubber-methyl methacrylate grafts.

Percentate methanol addition to 1% benzene solution of polymer

dissolving it in benzene and adding methanol containing a trace of ionic material. As illustrated in Figure 2, the free rubber precipitates out after about 20 per cent MeOH addition. Subsequent methanol addition causes the formation of a colloidal sol, in which the rubber chains are collapsed and show a white turbidity, but are kept in suspension by the solubility of the still extended methyl methacrylate side chains. When sufficient methanol (183 per cent) has been added to collapse these in turn, the sol is no longer stabilized, and the trace of ionic material present causes aggregation and the graft polymer fraction can be separated. After a further small methanol addition, the free polymethyl methacrylate separates. This method⁴ is of general application, and any such gross polymer mixture can be separated into its three components by using suitable solvent and precipitant.

It is now used for technological control of graft polymers as well as for isolating the pure grafts for special purposes. A simple modification serves for the rubber-styrene system. It should be emphasized that this separation depends entirely on the dual character of the graft, derived from two physically dissimilar

TABLE I
THE PREPARATION OF M-G 23

Ammoniated latex (60%)	100	} A
Water	100	
Ammonium caseinate	0.6	} B
Methyl methacrylate monomer (Kallodoc)	18	
Tertiary butyl hydroperoxide (75%)	0.18	} C
Tetraethylene pentamine (10% solution)	1.8	
Add B to A with stirring and then add C. Cease stirring, cover and leave 2 hours. Add		
Nonox-EXN (as 20% suspension in water made by ball-milling overnight with 1% Lubrol-W)	0.6	D
[Stir and pour into (boiling)		
Water	600	} E]
Formic acid (80-95%)	3	
Sheet on drying mill and dry below 80° C		

polymers. It is this same dual character which is responsible for some of the unusual technological properties.

Using this separative procedure, it was found that, with rubber, a profound difference in the products occurred when peroxidic catalysts and nonperoxidic catalysts (such as azoisobutyronitrile (AZBN)) were used. With the peroxidic catalysts grafting definitely takes place, the characteristic pattern being described below, whereas with AZBN there is virtually no grafting. This difference can easily be demonstrated by polymerizing two portions of a mixture of 10 per cent rubber and 90 per cent methyl methacrylate monomer with (a) 1 per cent benzoyl peroxide and (b) 1 per cent AZBN. The former gives a hard, translucent, very tough high-impact polymer, the graft acting as a mutual solubilizing agent; whereas the latter gives an opaque slightly tacky mixture of the free rubber and free polymethyl methacrylate which has no strength and readily shatters.

TECHNICAL PREPARATION

Most of the fundamental experiments with rubber were carried out in organic solvents, but for larger scale preparations polymerization in latex is much more convenient and accordingly will be dealt with here. The results correspond quite closely. Typical formulations⁶ are given below, using methyl

TABLE 2
THE PREPARATION OF S-G 35

Ammoniated latex (60%)	100	} A
Water	100	
Ammonium caseinate	0.6	} B
Styrene monomer	42	
Tertiary butyl hydroperoxide	0.25	} C
Tetraethylene pentamine (10% soln.)	2.5	
Add B to A with stirring, heat to 55° C. and add C. Cover and keep for 6 hours, at 55° C. Add		
Nonox-EXN (as 20% suspension in water made by ball-milling overnight with 1% Lubrol-W)	0.6	D
[Stir and pour into (boiling)		
Water	600	} E]
Calcium chloride	2	
Sheet on drying mill and dry below 80° C		

methacrylate and styrene. The peroxamine catalyst system chosen has the advantage that neither deaceration nor deammoniation is necessary.

The generic title Heveaplus has been given to these modifications of rubber with plastics, etc., the suffix M-G, and S-G indicating methyl methacrylate and styrene grafts, respectively, and the number giving the percentage of nonrubber polymer present, e.g., Heveaplus M-G 30 refers to a graft methyl methacrylate of composition 70 rubber 30 polymethyl methacrylate.

CONFIGURATION OF HEVEAPLUS GRAFTS

As an example, the M-G 23 whose preparation is described above has the quantitative configuration shown on the left hand side of Figure 3.

This pattern of long free polymer chains and very short multiple graft chains is characteristic of the use of peroxide catalysts. One result is that, even with

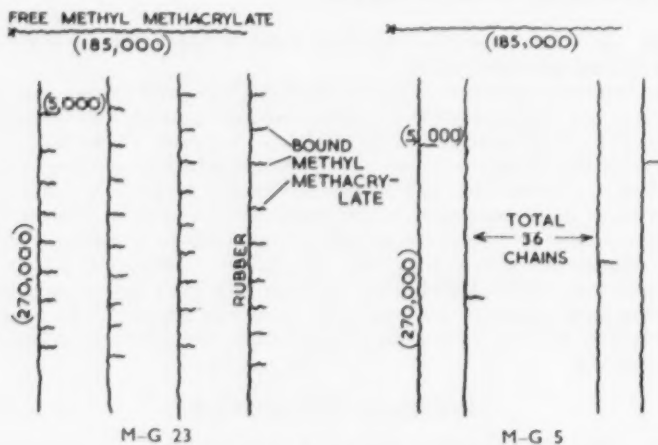


FIG. 3.—Detailed configurations of Heveaplus grafts.

as low as 5 per cent methyl methacrylate in the total polymer (see right hand side of Figure 3), there is still no residual free rubber.

The modified latexes prepared in this way can be used as such to produce reinforced cast films or foams⁴. This reinforcement does not occur with mixtures of rubber latex and polymethyl methacrylate latex. Alternatively, they can be converted, as indicated in the bracketed part of the formulae, into the modified dry rubber, whose utilization is described in the second part of this paper.

TECHNOLOGICAL PROPERTIES

INTRODUCTION

The main concern in this section of the paper is to summarize the technological properties of those polymer-modified natural-rubber compositions which are at present at the pilot plant stage of production and which are available to manufacturers in sample lots—namely, the graft methyl methacrylate, graft styrene and mixed methyl methacrylate types.

Some information on general properties has already appeared in print⁷, and

the data given here will of necessity review much that has been published previously. At the outset, however, it is felt necessary to emphasize the well recognized limitations of laboratory evaluations when dealing with any new material of this sort; the final decision must depend on the outcome of manufacturer assessment in practical applications and under factory conditions.

APPEARANCE, HANDLING AND COMPOUNDING

The appearance in the dry-rubber form is attractive, resembling a rather hard crepe rubber. Processing can be carried out readily on conventional equipment, and at 60° to 70° C the polymer component has softened sufficiently to make easy mixing, extruding, and calendering, even with materials which show a high degree of reinforcement in the final vulcanized condition. For concentra-

TABLE 3
COMPARISON OF HEVEAPLUS COMPOSITIONS BASIC FORMULATION

	Zinc oxide	5.0				
	Stearic acid	1.0				
	Sulfur	3.0				
	Accelerator	0.7				
	Antioxidant	1.0				
	N.R./H.A.F. tread	M-G23	M-M23	M-G30	M-M30	S-G35
Parts of total polymer	100	130	130	143	143	154
Tensile strength						
(kg./sq. cm.)	250	265	244	256	164	233
(lbs./sq. in.)	(3550)	(3775)	(3475)	(3650)	(2330)	(3315)
Elongation at break (%)	435%	553%	605%	490%	510%	493%
Modulus at 100% E						
(kg./sq. cm.)	30	29	30	46	49	40
(lbs./sq. in.)	(430)	(410)	(430)	(655)	(700)	(570)
Modulus at 300% E						
(kg./sq. cm.)	167	97	71	130	79	114
(lbs./sq. in.)	(2375)	(1375)	(1010)	(1850)	(1125)	(1620)
Modulus at 500% E						
(kg./sq. cm.)	—	230	179	—	162	—
(lbs./sq. in.)	—	(3275)	(2550)	—	(2305)	—
B.S.I. hardness degrees	71	70	77	82	90	87
Press cure at 140° C (min.)	25	20	20	20	20	20

tions up to about 35 per cent, the polymer constituent can be treated as an inert filler so far as compounding for vulcanization is concerned, and any conventional natural rubber systems, other than low-temperature acceleration, can be used. For polymer concentrations higher than 35 per cent, some additional sulfur and (or) accelerator may be necessary to obtain optimum physical properties.

Freedom from scorching is particularly pronounced, for example, a Santocure-accelerated stock which gave a Mooney scorch time at 120° C of 11 to 12 minutes in an HAF-loaded tread stock, gave 34 minutes in a compound of similar hardness and modulus based on Heveaplus M-G 23.

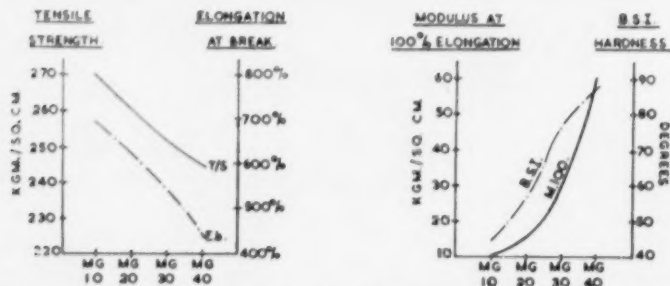
PHYSICAL PROPERTIES OF VULCANIZATES

Table 3 shows typical unaged physical properties obtained from Heveaplus vulcanizates compared with a natural rubber/high-abrasion furnace black-loaded tread stock. The main points to note are:—

- (1) The high tensile strength and breaking elongation of Heveaplus M-G 23 at tread hardness and modulus at 100 per cent elongation, but the lower modulus at 300 per cent elongation.
- (2) The higher hardness and modulus at 100 per cent elongation, but the lower tensile strength and modulus at 300 per cent elongation of mixed polymers when compared with graft polymers of similar concentration.
- (3) The lower degree of stiffening obtained with styrene-modified rubbers compared with equivalent methyl methacrylate modified compositions.

Behavior on oven aging is similar to that of natural rubber and there are no significant differences between the different modifying polymers in this respect.

Figure 4 illustrates the properties of Heveaplus M-G compounds directly prepared to cover a range of concentrations and indicates the high levels of tensile strength and breaking elongation which can be maintained even for



Base Mix—Zinc Oxide 5.0, Stearic Acid 1.0, Antioxidant 1.0, Accelerator 0.7 Sulphur 3.0.

M-G 10, 111 parts; M-G 20, 125 parts; M-G 30, 143 parts; M-G 40, 165 parts.

FIG. 4.—Tensile properties of Heveaplus M-G vulcanizates covering a range of polymer concentrations.

hardness values approaching 90 B.S.I. degrees. Present evidence suggests that there is no disadvantage as far as main physical properties are concerned in using high-concentration materials as masterbatch stocks and diluting with natural rubber to any desired level. Certain processing characteristics, e.g., ease of extrusion, may, however, be affected and in such circumstances it might be preferable to use materials directly prepared at approximately the concentration required in the final product.

BREAKDOWN AND MEMORY EFFECTS

If mastication of Heveaplus graft polymers either in the raw or in the compounded condition is carried out at temperatures above about 70° C, the behavior is similar to that of natural rubber in that both the stocks and the final vulcanizates soften with increasing breakdown. However, if the temperature is below 70° C, then, although the compounds soften, the vulcanizates become progressively harder and it is possible to cover the range from soft rubbery to stiff boardy materials by control of the breakdown conditions. Figure 5 shows the effect of cold breakdown and Figure 6 the effect of breakdown at different

temperatures for a styrene graft polymer of composition 65 rubber 35 polystyrene. The continuous fall of tensile strength and high-elongation modulus but the marked increase in hardness and low elongation modulus when cold breakdown is carried below about 30 Mooney viscosity, and the change from increasing to decreasing vulcanizate stiffness for breakdown temperatures above 70° C are evident.

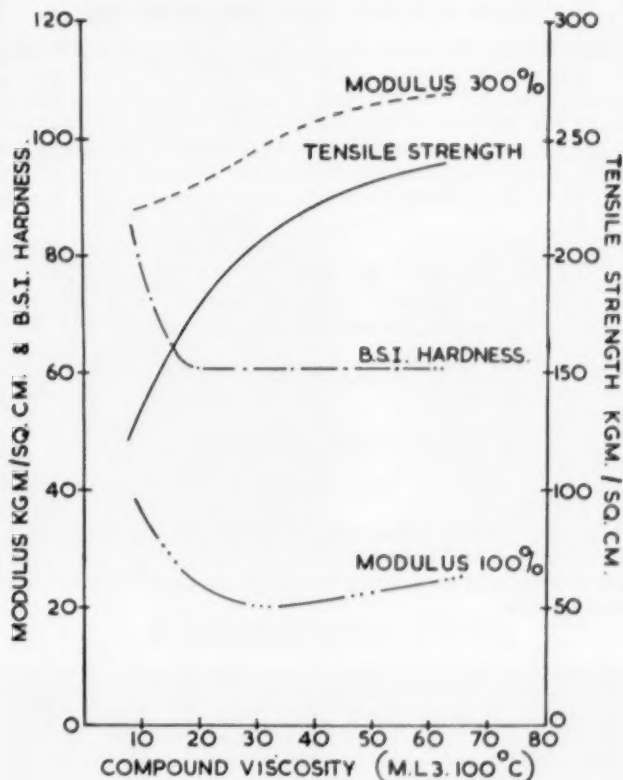


Fig. 5.—Effect of cold breakdown of a Heveaplus S-G 35 compound on vulcanizate properties.

A further difference from natural rubber is in behavior, which can conveniently be described as a memory effect similar to that exhibited by thermoplastics such as polystyrene or polymethyl methacrylate. If a vulcanizate is subjected to deformation, for example extension, and while held extended is heated above 100° C, and then let cool again, there will be no retraction on release, and the extended length is maintained indefinitely at room temperature. However, on raising the temperature again, retraction will take place until the original undeformed condition is regained (Figure 7). These effects are particularly marked with high-concentration polymers and with stocks which have been subjected to heavy cold breakdown.

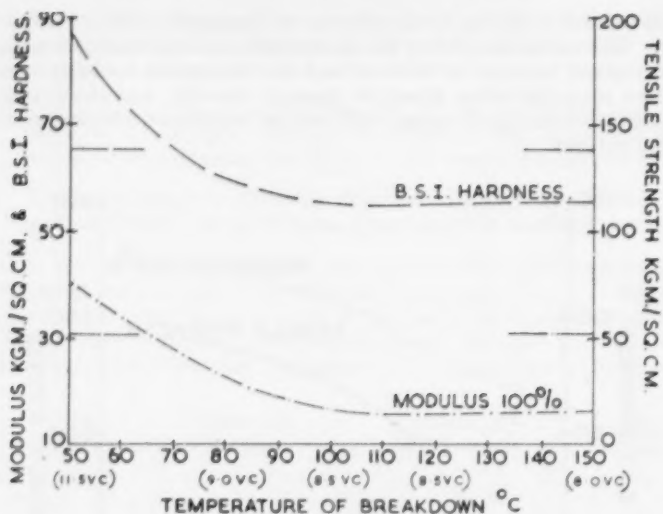


FIG. 6.—Influence of breakdown temperature on the stiffness of a Heveaplus S-G 35 vulcanizate.

ADDITIONAL PROPERTIES

TEAR STRENGTH

This is good at normal temperatures but, as might be expected, both tear and tensile strength fall off as the temperature rises and the reinforcing polymer constituent softens, and at molding temperatures care is needed in removing complicated sections.

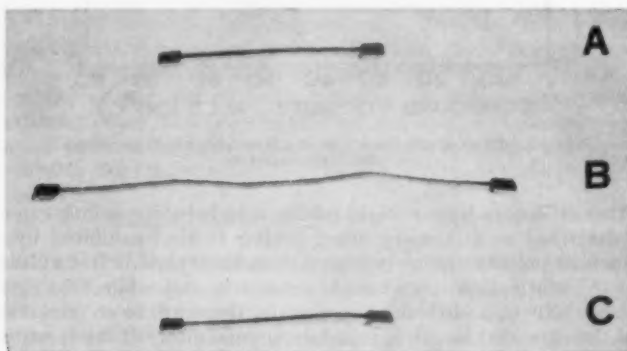


FIG. 7.—Memory effects in Heveaplus compounds.

- (A) Original sample.
- (B) Stretched at 120° C and let cool in the stretched state.
- (C) Reheated to 120° C to allow free retraction.

ABRASION RESISTANCE

At tire-tread hardness, the abrasion resistance of a Heveaplus M-G compound is intermediate between the equivalent HAF black and MPC black-loaded stocks giving a volume loss per 1000 rev. of around 0.250 cc. when tested on the Akron abrasion machine.

RESILIENCE, HYSTERESIS, AND HEAT BUILD-UP

Dunlop Tripsometer rebound, measured at room temperature on Heveaplus M-G at a hardness level of 70 B.S.I. degrees, is of the order of 70 to 75 per cent, and this high value is reflected in low hysteresis and low heat build-up, providing the operating temperatures are not excessive and both the amplitude and frequency of the deformations are low. Under more severe service conditions, the difference compared with normal natural-rubber compounds is less marked, and with very high temperatures and deformations they may in fact be reversed.

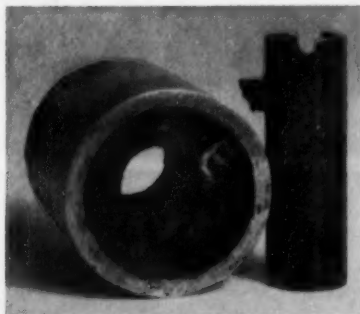


FIG. 8a.



FIG. 8b.

Bonded bush units.

- (A) Black loaded N.R. bush after 60,000 cycles.
(B) Heveaplus M-G bush after 3,000,000 cycles.

A possible utilization of these improved dynamic characteristics is in the field of bonded bush units. Figure 8 shows a conventional black-loaded natural-rubber bush after 60,000 cycles of a deformation 20° either side of zero at the rate of 120 per minute, compared with a bush prepared from Heveaplus M-G after 3,000,000 cycles under similar conditions.

FLEX CRACKING AND CUT GROWTH

These properties are ones where the laboratory test data are difficult to interpret in terms of likely service performance. If tests are carried out with Heveaplus M-G at reinforcement levels equivalent to normal tire treads, using the de Mattia machine to B.S. 903, no flex cracking is apparent in the time for complete failure of black-loaded stocks. Under more severe flexing conditions, genuine flexing may be masked by the development of edge cuts, which may ultimately cause failure. The behavior of a deliberately initiated cut is also peculiar in that initial growth is very rapid, after which the cut seals off, and no further growth is apparent on subsequent flexing. In consequence, the ranking in relation to conventional filled compounds will be determined by the stage at

which the comparison is made. Figure 9 compares natural-rubber tread stocks containing MPC and HAF blacks with a Heveaplus M-G tread after 10^6 cycles on the de Mattia, the top row showing flexing and the bottom row cut growth. Under these conditions of comparison, the Heveaplus compound appears outstanding, but service life would undoubtedly depend on the actual conditions involved.

CONCLUSIONS

This brief survey of the technological properties of the polymer-modified natural rubbers which have so far been developed to the pilot plant stage is intended mainly as a guide to possible applications. Obvious fields of interest for the dry rubber include molded and extruded articles covering the range from the rigid to the elastic state, coupled with a high degree of reinforcement and the possibility of obtaining transparent, translucent, or colored vulcanizates if

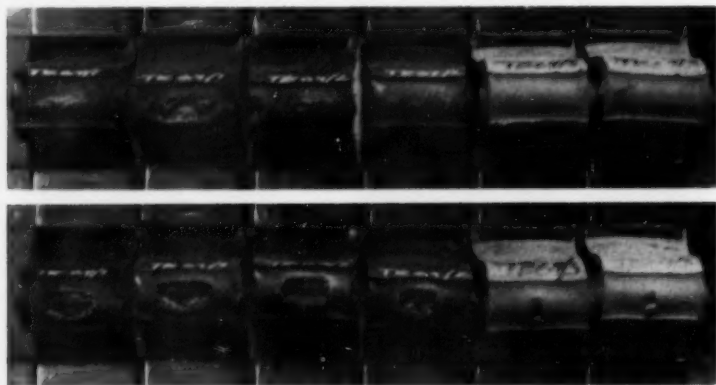


FIG. 9.—Flex cracking and cut-growth behavior 1,000,000 cycles on the de Mattia. Top: Flex cracking. Bottom: Cut growth. 1st pair, M.P.C. tread. 2nd pair, H.A.F. tread. 3rd pair, Heveaplus M-G tread.

desired. Recent developments based on manufacturer evaluations indicate that the main interest at present may center on higher concentration materials, either alone or with additional fillers, giving hard rigid vulcanizates, which by virtue of the thermoplastic nature of the reinforcing constituent, still retain excellent processing properties, particularly with regard to molding behavior.

Applications in the latex field have not been touched on, mainly because there are many problems still unsolved, but one potential use is in the production of foams of similar bulk density but of greater stiffness than natural rubber foams, the stiffness still being retained after repeated deformation.

In conclusion, the materials which have been discussed should not be looked on as the final word in modified rubbers, but simply as the first step towards the use of natural rubber as a basic raw material for the production of so called tailor-made polymers.

SUMMARY

Earlier efforts to prepare and examine rubber-synthetic polymer compositions have made virtually no attempt to determine the nature of the products, that is, whether they were simple mixtures or chemical compounds and, if the

latter, of what type, and thus to rationalize, if only broadly, their physical and technological properties in terms of their basic structures. The work now described has had this object in mind, and represents a cooperative program of research, including chemical, physical, and technological aspects.

ACKNOWLEDGMENT

This work forms part of a program of research undertaken by the Board of the British Rubber Producers' Association.

REFERENCES

- ¹ Bawn, "The Chemistry of High Polymers", Butterworth, 1948, p. 70.
- ² Scanland, *Trans. Faraday Soc.* **50**, 756 (1954).
- ³ Merrett, *Trans. Faraday Soc.* **50**, 759 (1954).
- ⁴ It has since been found that the graft polymer is capable of solubilizing a considerable quantity of free rubber, so precipitation of this free rubber does not occur where expected in the above scheme. Thus when benzoyl peroxide is used as initiator, the amount of graft polymer produced is sufficient to solubilize the residual free rubber in rubber-methyl methacrylate reaction products containing 10 per cent or more vinyl polymer. Larger amounts of free rubber, when, for example, AZBN is used, separate as expected. It is, therefore, necessary to supplement the above separation by an extraction with petroleum ether or a mixture of benzene and petroleum ether in order to remove all the free rubber. The separation of the free vinyl polymer is independent of this effect and can be made before or after the petroleum-ether extraction. This solubilization of free rubber into the graft polymer fraction had the effect that the grafted vinyl polymer was apparently attached to many more rubber chains than was the fact and, hence, that the individual attached chains seemed shorter. Our most recent results indicate that the free and grafted vinyl polymer chains grow to approximately the same length.
- ⁵ Bloomfield, Merrett, Popham, and Swift, *Proc. Third Rubber Technol. Conf.*, 1954, p. 185.
- ⁶ Cockbain and King, unpublished work.
- ⁷ British Rubber Producers' Research Association, Techn. Bull. No. 1, "Heveaplus M", issued by the British Rubber Development Board.

MECHANICAL PROPERTIES OF POLYMERS IN THE RANGE OF THEIR SOFTENING. ELONGATION DIAGRAMS OF RAW AND VULCANIZED RUBBER *

N. A. YUZEFOVICH AND E. V. KUVSHINSKIĬ

A study of the mechanical properties of polymers through the softening range is interesting for two reasons: on the one hand, it throws light on the process of vitrification, and, on the other, a study of reactions at low temperatures can give at least qualitative indications of the behavior of a material at high temperatures and during rapid dynamic processes, i.e., under conditions where direct investigation involves considerable difficulties in the experimental method.

The following substances were studied: unloaded butadiene rubber before and after vulcanization, and vulcanized natural rubber. The temperature range studied was -100° to 20° C.

The elongation diagrams were obtained by means of a mechanism constructed in our laboratory. The specimens were stretched in a temperature-controlled chamber. Variations of temperature below 0° C did not exceed 0.5° C, and above 0° C did not exceed 0.2° C. The deforming force F was measured with a spring ring dynamometer. The opening of the clamps was calibrated with respect to the relative elongation λ . A correction was introduced here for deformation of samples in the clamps. The use of a reducing mechanism made it possible to vary the rate of deformation within the limits $v = 0.0016$ and 0.08 cm. per sec., corresponding to rates of deformation from 0.05 to 2.5 per cent per second.

The specimens were of the dumbbell type (length of measured section: $l_0 = 2.5$ cm. and cross-section $S_0 \sim 0.036$ sq. cm.). Furthermore, a number of measurements were made on ring-shaped specimens (outside diameter 3.2 cm.; cross-section $S_0 = 0.05$ sq. cm.).

After being tested, each specimen was kept at room temperature for a long time. A piece was cut out of the uniform part and its length and weight were measured. From these values, and knowing the density of the material, the initial cross-section of the specimen, S_0 , could be calculated.

On the basis of the experimental data, deformation curves were constructed in the form of the relations: $f = f(\lambda)$ and $\sigma = \sigma(\lambda)$, where $f = F/S_0$ is the specific load (conventional stress), and $\lambda = l/l_0$ is the relative elongation. $\sigma = F/S = F \cdot l/v \approx (F/S_0)\lambda$ is the stress (disregarding changes of the volume of the material during deformation).

Diagrams of the deformation of vulcanized butadiene are shown in Figures 1a and 1b. At temperatures between -28° and 20° C, the stress σ increases smoothly with the elongation. The lower the temperature, the steeper are the curves. When the material begins to harden, phenomena of forced elasticity

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Zhurnal Tekhnicheskoi Fiziki* S.S.S.R., Vol. 23, No. 8, pages 1343-49 (1953).

are observed. At temperatures $\leq -42^\circ\text{C}$, the laws change abruptly. A peak appears on the initial segment of the diagram of stretching ($\lambda \approx 1.05$ to 1.15), the value of which increases with a decrease of temperature. After the fall of stress beyond the peak, a gradual increase of stress with elongation again takes place. This segment of the diagram is not always uniform. Often local breaks and jumps are observed. After the load is removed, the specimens remain in a deformed state. It is sufficient only to heat them gently, and their rubberlike elasticity is restored, and they shrink to their original size. No irreversible changes or interruptions in the structure of a polymer were observed during elongation at low temperatures (for example, at temperatures of -45 to -40°C up to $\lambda = 3$ to 4). If the specimens are again cooled and stretched a second time, the diagram of repeated deformation differs slightly from that obtained

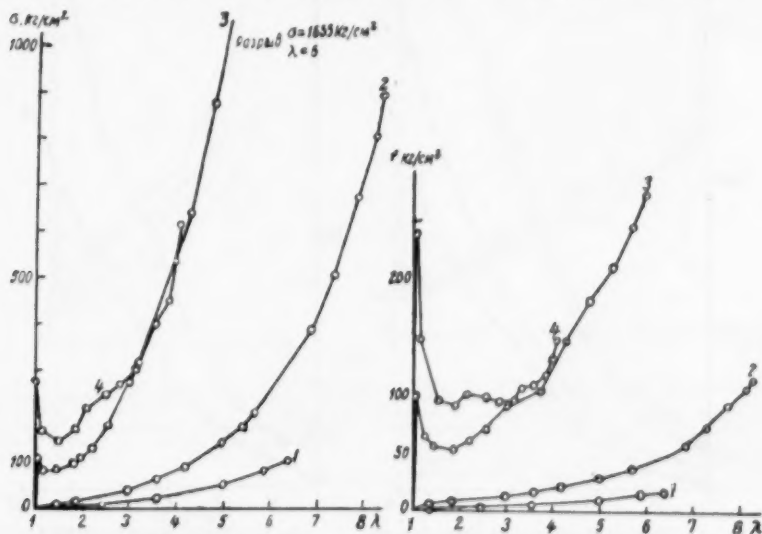


Fig. 1.—Effect of temperature on deformation curves of vulcanized polybutadiene. 1. 19.5°C ; 2. -28.2°C ; 3. -42.1°C ; 4. -45.0°C . Rate of stretching 2.5% per second.

in the first experiment. Sometimes small deflections appear in the first stages of deformation; these disappear during further elongation. The formation of deflections cannot be a cause of the appearance of peaks, if only because such peaks are also observed during compression, when no deflections are observed. On the other hand, it is easy to show that the presence of a peak, or rather a section in the diagram of stretching where the strain falls with further stretching, facilitates irregular longitudinal deformation of the specimen, that is, the appearance of a deflection.

The decrease of stress during deformation can not be related to the initial heating of the specimen. In the initial stage, where the tension increases with elongation, the work of deformation, and, consequently, heating of the specimen, is slight. The temperature hardly ever increases, even under complete adiabatic conditions, more than 0.1 to 0.3°C .

The shape of the deformation curves is essentially dependent on the rate of stretching; an increase in the latter is qualitatively equivalent to a decrease in

the experimental temperature. In fact, experiments with vulcanized butadiene at $0 \approx 42$ to 45°C (Figure 2) showed that the nature of the curves is entirely different at different deformation rates. If, when the rate of elongation is 0.05 per cent per second, we observe a steadily increasing stretching curve, then, when the elongation is 2.5 per cent per second, the curve has the characteristic peak of the initial stage. Consequently, the time-relaxation processes play an important role in the phenomena observed in the range of induced elasticity. The stresses which develop in the specimen during stretching at a low rate can be resolved to a large degree. Hence at low rates of deformation, the peaks

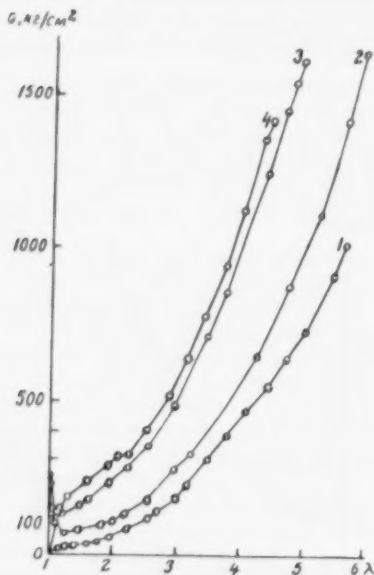


FIG. 2.—Effect of temperature and rate on deformation curves of vulcanized polybutadiene. 1. -42.9°C . Rate 0.5% per sec. 2. -42.1°C . Rate 2.5% per sec. 3. -48.5°C . Rate 0.05% per second. 4. -50.0°C . Rate 0.05% per second.

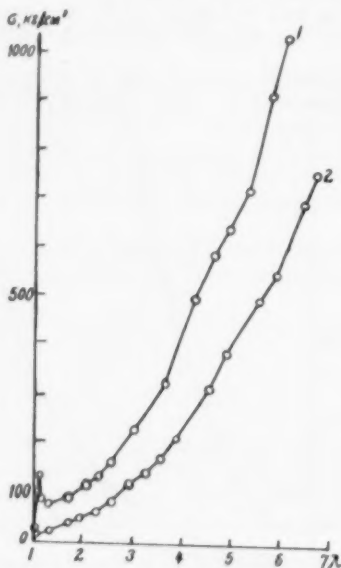


FIG. 3.—Effect of rate on deformation curves of raw polybutadiene. 1. -45.6°C . Rate 2.5% per second. 2. -45.3°C . Rate 0.05% per second.

appear only at lower temperatures. The change of rate of deformation from 2.5 to 0.05 per cent per second is equivalent to a decrease of temperature of about 5° to 8°C .

All the peculiarities of the elongation diagram observed in the range of vitrification appear in vulcanized rubbers as well as in raw rubbers (Figures 3 and 4). Experimental data from dumb-bell and ring-shaped specimens is shown in Figure 4. A comparison of the data shows that the law is the same in all cases; only in the ring are the stresses somewhat lower. This is evidently due to the fact that the ring is not uniformly loaded. The outer layers are deformed comparatively more than the inner layers, which smoothes out the top of the peaks and, in general, evens out the entire deformation curve. A number of experimental data from specimens vulcanized to various degrees are shown in Figure 5. As is seen, the curves do not differ greatly for raw and vulcanized butadiene rubber. Consequently, the existence of a spatial network, due to

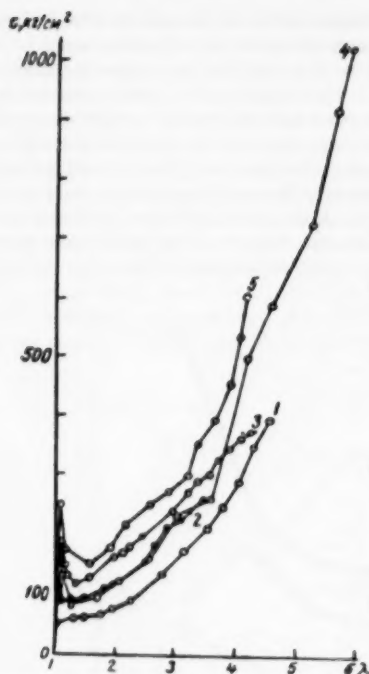


FIG. 4.—Effect of temperature on deformation curves of raw and vulcanized polybutadiene. Rings: 1. -46.2°C (raw); 2. -45.4°C (vulcanized); 3. -44.5°C (vulcanized). Dumb-bell shaped: 4. -45.6°C (raw); 5. -45.0°C (vulcanized). Rate 2.5% per second.

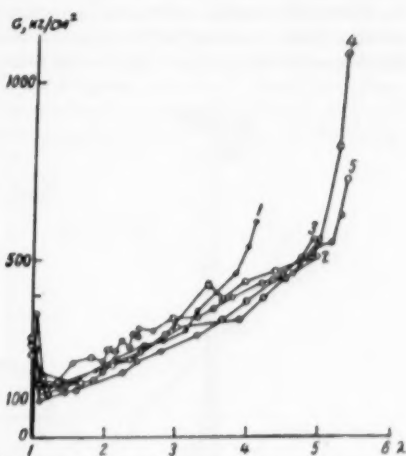


FIG. 5.—Effect of vulcanization on deformation curves at low temperatures. 1. -45.0°C , vulcanized 40 minutes at 143°C ; 2. -45.6°C , vulcanized 40 minutes at 143°C ; 3. -45.0°C , vulcanized 40 minutes at 120°C ; 4. -48.0°C , vulcanized 20 minutes at 120°C ; 5. -47.1°C , vulcanized 10 minutes at 120°C . Rate 2.5% per second.

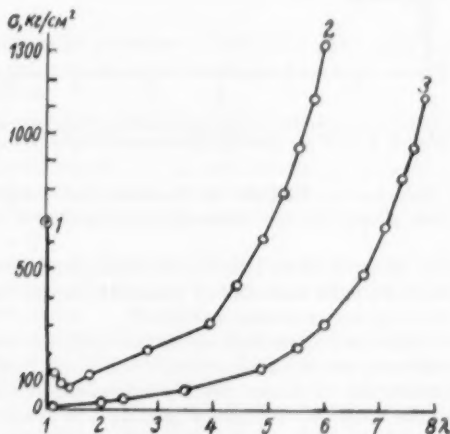


FIG. 6.—Effect of temperature on deformation curves of vulcanized natural rubber. 1. -70.6°C ; 2. -66.8°C ; 3. -57.3°C . Rate 2.5% per second. Vulcanized 20 minutes at 120°C .

cross-linking, of the separate linear molecules with vulcanization bridges has little influence on the properties of the material in the vitrification range.

The shape of the deformation curves in the vitrification range is unusual not only in the case of butadiene rubber. The experimental data presented in Figure 6 show that, in the case of vulcanized natural rubber in the range of vitrification, the same characteristic peaks are observed in the initial sections of the curves. The only difference between this case and that of vulcanized butadiene rubber is that the peaks are observed here at lower temperatures.

The deformation curves of plastics, such as acetylcellulose, polymethylmethacrylate and polystyrene, have a similar shape¹. The latter two substances were studied in considerable detail by Lazurkin and Fogelson². In our



FIG. 7.—Effect of temperature on deformation curves of polyvinyl acetate. 1. 41.2° C; 2. 37.6° C; 3. 37.6° C. Specimen first tempered at 100° C in a thermostat.

laboratory, G. A. Lebedev studied the mechanical properties of polyvinylacetate films. He also observed the characteristic peaks of the deformation curves (Figure 7).

It is necessary to bear in mind that it was with plastics—polystyrene and methylmethacrylate—that the existence of peaks on the curves of compression as well as those of elongation was demonstrated³.

The analogous behavior of raw and vulcanized rubbers and plastics (polyvinylacetate, polystyrene, methylmethacrylate, acetylcellulose) shows that the laws observed characterize all linear weakly side-chained and weakly cross-linked polymers in the range of "induced elasticity", as it was called by Aleksandrov⁴. This reflects the structural peculiarities and intermolecular reactions common to the whole class of polymers indicated.

As has been shown previously, raw and vulcanized rubbers at low temperatures lose most of their capacity for spontaneous shrinkage. Data for raw butadiene are shown in Figure 8. The load was removed twice during the experiment, the results of which are shown in Figure 8a. In both cases, only slight shrinkage of the specimen was observed after release of the load. A completely unstressed specimen shrank very slowly. Restoration of the deforming force brought the specimen back to the original curve. The deformation curve obtained when stretching was periodically interrupted and the specimen was held in the deformed state is shown in Figure 8b. Rapid relaxation of stress was observed from the moment when deformation ceased. At $\lambda = 1$ to 1.5, the stress fell 8 to 10 times in 2 to 3 minutes. At $\lambda > 2.5$, the fall of stress was not so rapid: to 20 to 30 per cent of the original value in 10 to 15 minutes. After renewed deformation, as in the preceding experiment (Figure 8a), the stress rapidly reached the value corresponding to that of continuous deforma-

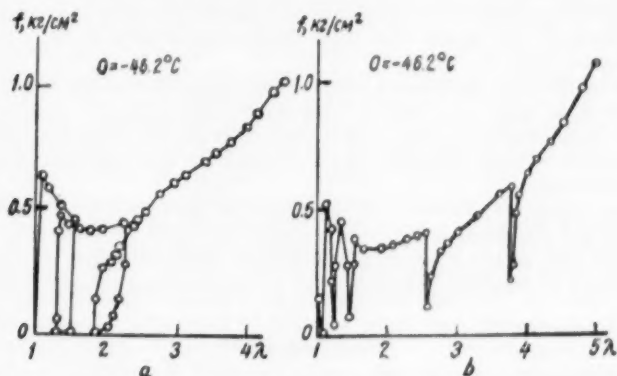


Fig. 8.—Relation of specific loads to relative elongation of raw polybutadiene rubber rings. Rate 2.5% per second.

tion. Consequently, the processes which cause the comparatively rapid relaxation of stress do not greatly affect the behavior of a material during subsequent deformations.

It is worthy of note that the relaxation of stress was also observed when the initial stage of deformation was interrupted before the maximum value of the stress was reached at the peak. This contradicts the statement of Lazurkin and Fogelson² that, at the beginning of deformation, the material behaves like a perfect elastic and the relaxation processes take place only when the stress peak is reached.

The disappearance of the peaks when the rate of deformation is reduced (Figures 2, 3) also attests to the fact that there is no purely elastic initial section of the deformation curve.

Some long-lasting processes which accompany the fairly constant low residual stresses retained by the deformed material have a very different effect. They lead to stiffening of the material. Restoration of deformation after a long interval again shows a stress peak. The specific load in the second peak when $\lambda \sim 2$ to 2.5 always has a lower value than the first peak in the range $\lambda \sim 1.05$ to 1.10, while the values of the stress at the peak are the same or

higher in the second peak. After a long interruption at $\lambda > 3.5$, that is, in the range where the stresses during continuous deformation are greater than the stress at the peak for $\lambda = 1.05$ to 1.10, if the experimental temperature and the rate of deformation are constant, no peak is observed.

At the present time, it is difficult to explain all the observed phenomena. Undoubtedly the peculiarities of the deformation curves reflect the nature of the molecular processes which accompany the deformation of linear weakly cross-linked polymers, such as regroupings of the polymer chains. The latter is noticeable only under considerable external mechanical influences. When the stress is removed, these reactions are irreversible. Only at high temperatures can heat transfer rapidly restore the original orientation of the molecules. It is possible that these regroupings are localized principally in the chains or the ends of the chains, which interpenetrate the individual molecular conglomerates. It is these reactions which must serve primarily as an obstacle to unwinding and stretching out most of the polymer chains formed at great deformations. Hence, at deformations $\lambda > 3.5$ the intersecting effect becomes less pronounced, and the peaks do not appear even after the specimens are kept for a long time in a deformed state.

It is seen that the phenomena which accompany deformation of polymers in the vitrification range are complex, and can not be subsumed simply as a decrease of elastic relaxation time with stress. It is clear that the ideas expressed by Aleksandrov⁴, upon which the work of Lazurkin and Fogelson² was based, are too schematic.

In conclusion, we observe that the nature of the mechanical effects which determine the vitrification temperature must be carefully analyzed. In the light of our data on the mechanical behavior of linear polymers, it is not possible at present to establish precisely what is, in fact, being measured in a given case.

BIBLIOGRAPHY

¹ Alfrey, *Mekh. Svoistva Vysokopol.*, II, 1952.

² Lazurkin and Fogelson, *Zhur. Tekh. Fiz.* 21, 267 (1951).

³ Lazurkin and Fogelson, *Zhur. Tekh. Fiz.* 21, 267 (1951); Alfrey, *Mekh. Svoistva Vysokopol.*, II, 1952.

⁴ Aleksandrov, *Trudy I and II Konferentsii po Vysokomol. Soedineniam, Akad. Nauk S.S.S.R.* 1945, p. 40.

A COMPARISON OF THE DYNAMIC PROPERTIES OF NATURAL RUBBER AND GR-S *

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INTRODUCTION

It is well known that high molecular weight, uncross-linked, amorphous polymers show a characteristic behavior with respect to the dependence of the dynamic modulus on frequency and temperature¹. Generally these materials, at high frequencies and (or) low temperatures, are glasslike, with a modulus of approximately 10^{10} dynes/cm.². As the frequency is lowered or the temperature raised, this modulus drops rather quickly to the region of 10^6 to 10^7 dynes/cm.², and remains in this neighborhood for a while to form somewhat of a plateau, the length of which depends on the molecular weight. With a further lowering of frequency or rise of the temperature, the modulus again drops off in a fashion which is strongly dependent on the molecular weight and molecular-weight distribution and the material enters a plastic or liquid-like region. This general behavior seems to be characteristic of long-chain molecules in general, and differences in structure are more likely to be reflected in differences of detail, and in the temperature ranges in which the afore-mentioned regions occur, than in any considerable divergence from the general pattern. A comparison between the dynamic properties of the two important elastomers, GR-S and natural rubber, is here reported. In preliminary work in this laboratory, it has been observed that GR-S shows an appreciably higher level for the plateau region than natural rubber. It was felt that this and other possible differences between the two materials would merit exploration, particularly for any implication that the results might have for the long-standing problem of the origin of the tendency of GR-S to show a greater development of heat under repetitive stressing than natural rubber.

EXPERIMENTAL

The high molecular weight end of a rough fractionation of a GR-S containing 20 per cent bound styrene was used. This was prepared in a standard recipe at 50° C at the Government Laboratories, University of Akron. The natural-rubber sample also was the high-molecular cut of a sample of crepe rubber. The viscosity-average molecular weight of both samples was something over a million. Sheets were solvent-cast from benzene solutions and rectangular samples died out. Several such samples were placed together to give a thickness best suited for the temperature range under investigation. It was, in general, necessary to use several samples of different thicknesses in order to bring the measurements within the range of the instrument.

The instrument used for the measurements has been described more in detail elsewhere². In brief, it is a torsion pendulum operated electrically in

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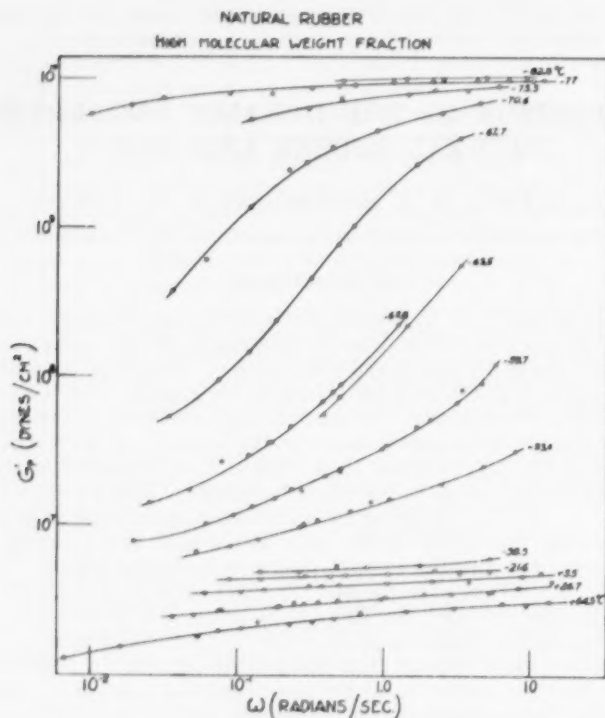


FIG. 1.—Real part of reduced dynamic modulus of natural rubber as a function of frequency.

forced vibration from a low-frequency sine wave generator. Measurements consist chiefly of a determination of the relative amplitudes of the driving force and the sample response and of the mechanical phase angle between them. The instrument is housed in an air thermostat, which permits the regulation of the temperature at any place between -80 and $+100^{\circ}\text{C}$. The frequency range was from 2 cps to 5×10^{-2} cps. Some difficulty had been anticipated from crystallization in natural rubber at temperatures of -10 to -30°C , but none was encountered. It is presumed that the length of time (one to two hours) that the sample remained in this temperature range was not sufficient to permit an appreciable amount of crystallization.

RESULTS

The data are obtained in terms of G' and G'' , the real and imaginary parts of the complex modulus. From these the corresponding compliances, J' and J'' , may be calculated from the expressions:

$$J' = G' / [(G')^2 + (G'')^2]$$

and

$$J'' = G'' / [(G')^2 + (G'')^2]$$

Moduli were reduced for temperature by the method suggested by Ferry³, whereby the limiting, low-temperature, glass compliance, J'_{∞} , is subtracted out of the real part of the compliance before the usual temperature reduction is made. Thus:

$$J'_p = J_{\infty} + (J' - J_{\infty})(T\rho/T_0\rho_0)$$

and

$$J''_p = J''(T\rho/T_0\rho_0)$$

where the subscript p denotes the reduced quantity, ρ is the density of the sample at the temperature T , and ρ_0 is the density at the reference temperature T_0 . The reduced moduli are then obtained from:

$$G'_p = J'_p / [(J'_p)^2 + (J''_p)^2]$$

and

$$G''_p = (J''_p) / [(J'_p)^2 + (J''_p)^2]$$

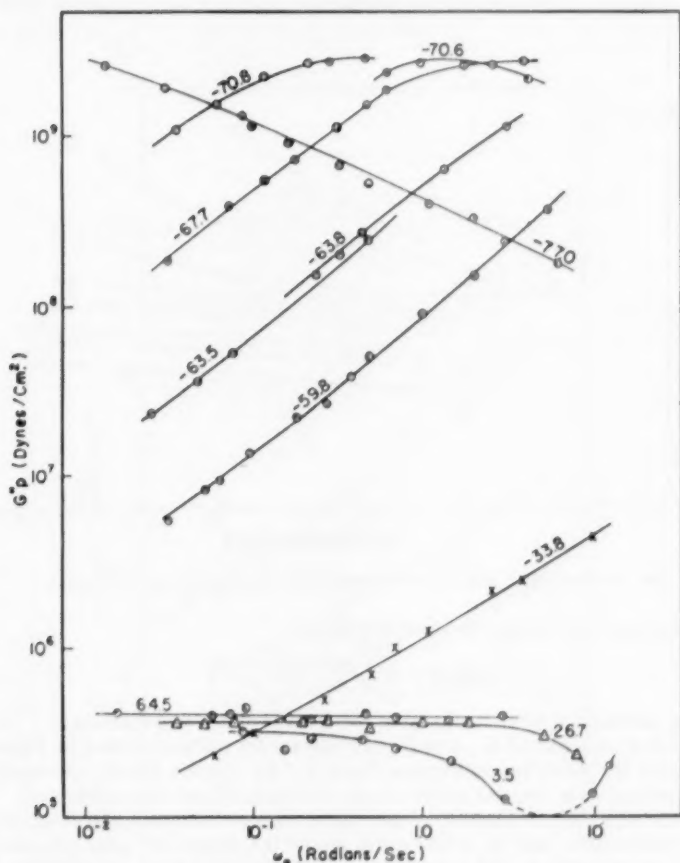


FIG. 2.—Imaginary part of reduced dynamic modulus of natural rubber as a function of frequency.

UNVULCANIZED GR-S
HIGH MOLECULAR WEIGHT FRACTION

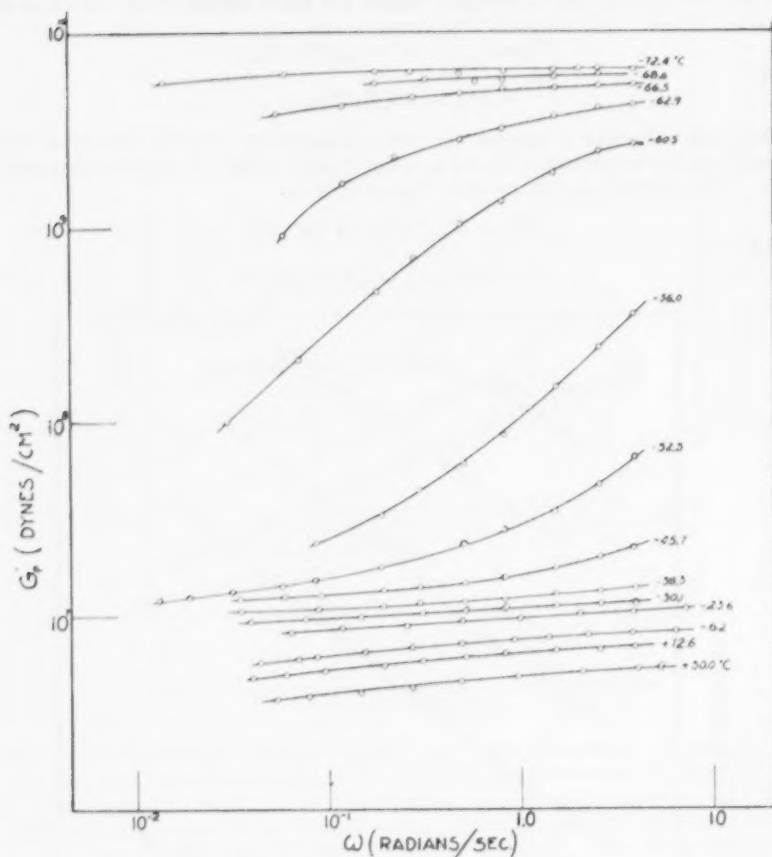


Fig. 3.—Real part of reduced dynamic modulus of GR-S as a function of frequency.

Reduced loss factors may be obtained from:

$$\tan_p \delta = G''_p / G'_p = J''_p / J'_p$$

Density corrections were made using the data of Witte and Anthony⁴.

The reduced moduli G'_p and G''_p are shown for natural rubber in Figures 1 and 2, and for the GR-S in Figures 3 and 4. By shifting the G'_p curves along the frequency axis, the composite curves shown in Figure 5 are obtained. The frequency axis is the reduced frequency, ωa_T , where ω is the angular frequency of the measurement and a_T is the shift along the frequency axis necessary to achieve superposition. The same type of shifting can be done with the G''_p , and the results of this are shown in Figure 6 for both materials.

The shifting factors a_T are the temperature coefficients of the relaxation times, and it is to be expected that the same values would be obtained from shifting either the G'_p or the G''_p values, and that:

$$\tan \delta = G''_p / G'_p$$

should also superpose using these same a_T values. $\tan \delta$ for both materials are plotted in Figure 7 against the reduced frequencies based on a_T obtained from the shifting of G'_p . The results are just fair. There seem to be some irregularities in the neighborhood of the steep rise of modulus that occurs as the apparent second-order transition region is entered. There is also some evidence that heights of the $\tan \delta$ peaks, as a function of frequency, are not independent of temperature. Whether or not these irregularities are significant with respect to a failure of the superposition procedure is not certain. In the case of $\tan \delta$, they may merely reflect a greater sensitivity of the loss factor to inaccuracies in the data.

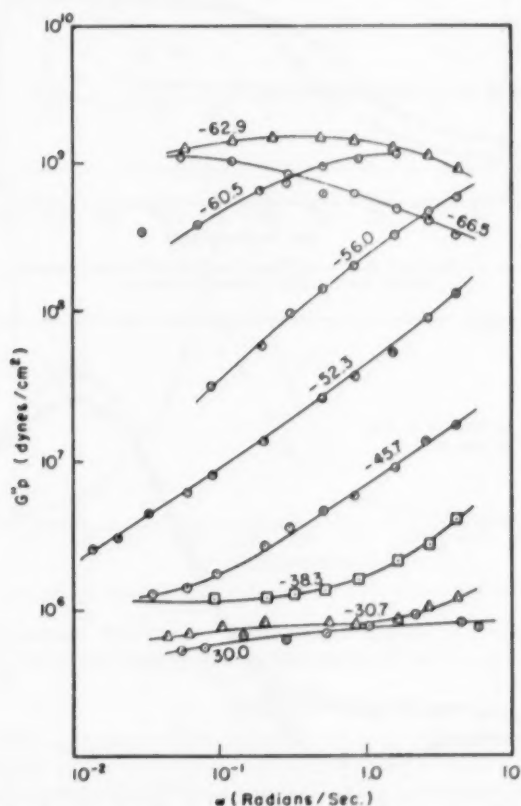


Fig. 4.—Imaginary part of reduced dynamic modulus of GR-S as a function of frequency.

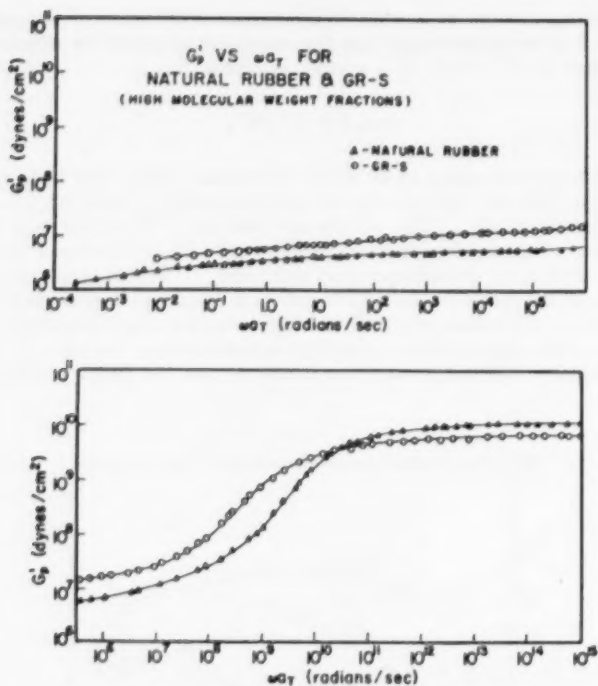


FIG. 5.—Real part of reduced dynamic moduli of GR-S and natural rubber as a function of reduced frequency.

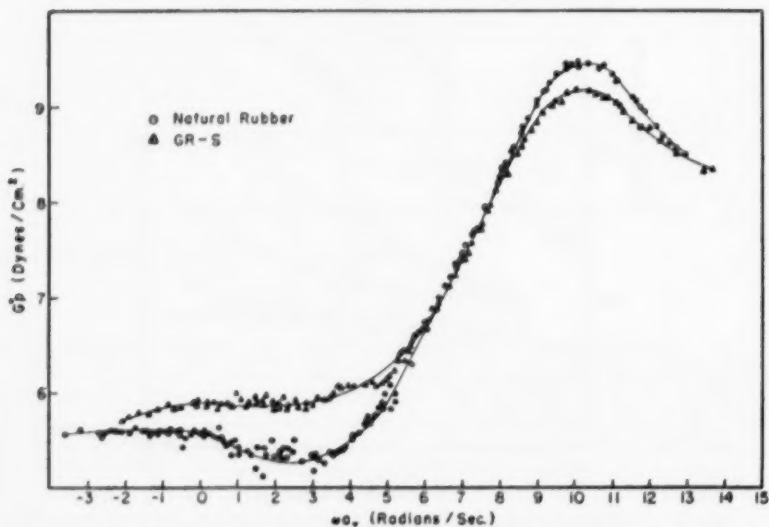


FIG. 6.—Imaginary part of reduced dynamic moduli of GR-S and natural rubber as a function of reduced frequency. Both the ordinate and the abscissa are in log values.

The logarithms of the a_T values obtained independently from the shifting of both G'_p and G''_p are plotted against $1/T$ in Figures 8 and 9 for natural rubber and GR-S, respectively. Agreement between the two sets of data for GR-S is quite adequate but, in the case of natural rubber, there is some discrepancy, and again there is a suggestion that the superposition procedure may require some reexamination.

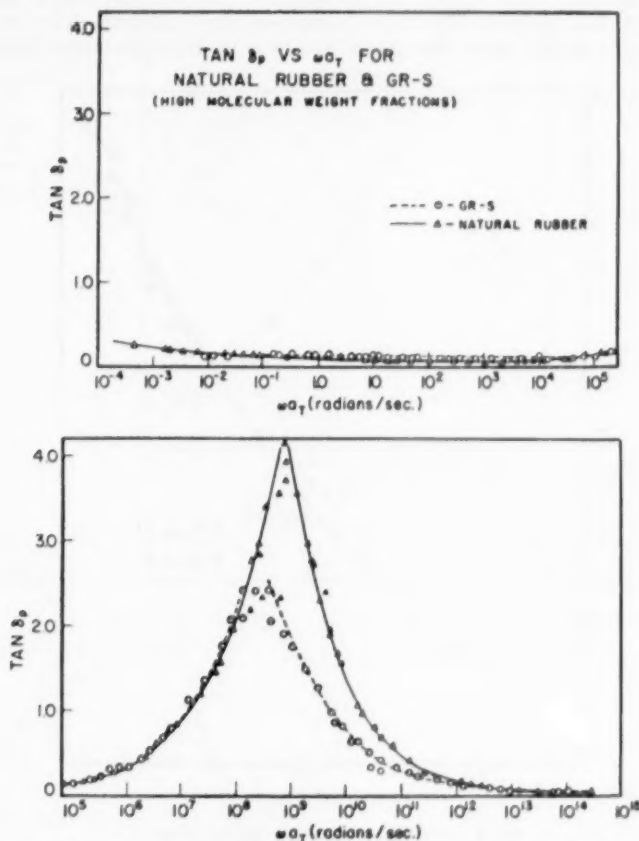


FIG. 7.—Reduced loss factor for GR-S and natural rubber as a function of reduced frequency.

The distribution function of relaxation strengths, computed from the G'_p curves using Ferry's second approximation method⁶, is shown for both materials in Figure 10.

DISCUSSION

An interesting feature of this comparison between natural rubber and GR-S is the similarity in their dynamic behavior, a result perhaps not unexpected in the light of accumulating experience with other polymer systems. Natural rubber has a lower apparent second-order transition temperature than GR-S, and the transition region, judging from $\tan_p \delta$ curves, seems somewhat sharper. The low temperature, limiting glassy modulus is higher (1.1×10^{10} dynes/cm.²)

for natural rubber than for GR-S (6.6×10^6 dynes/cm.²). On the other hand, the modulus in the rubbery plateau region is higher in the case of GR-S. The existence of this region may result from the presence of coupling between chains, which confer a quasi-network character on the material reminiscent of a gel. If so, such coupling must be higher in GR-S than in natural rubber. The bonds involved must be either of a van der Waals nature or the result of entanglements. In any case, they relax readily and the effective modulus drops off at low frequencies, unless a network of more permanent chemical cross-links has been introduced. In the latter case, there will be a modulus associated with this

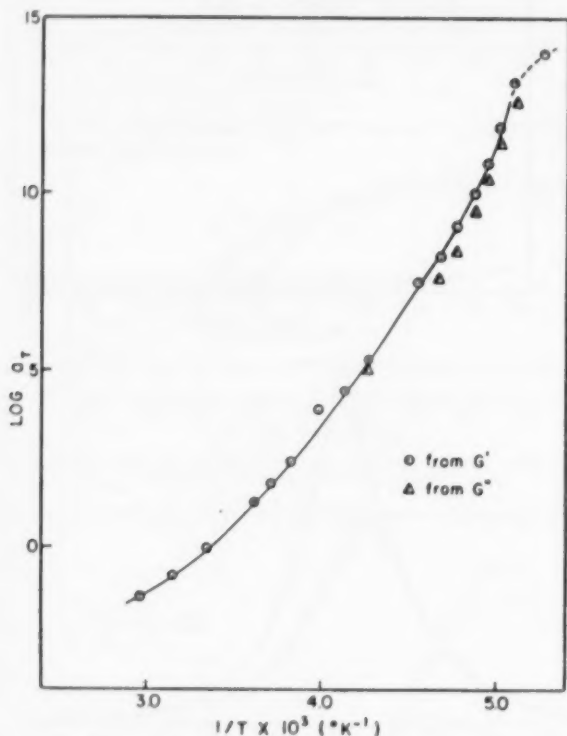


FIG. 8.—Plot of $\log a_T$ vs. $1/T$ for natural rubber.

latter network and, if it is lower than that of the temporary gel-modulus characteristic of the material, a modulus dispersion will result; increased dynamic losses always result from such a dispersion. It is suggested that this may be at least a contributory factor, and may be a major one, to the undesirable loss characteristics of GR-S. For example, if natural rubber is vulcanized to a given degree, say equivalent to a permanent network modulus of $3-4 \times 10^6$ dynes/cm.², the gel modulus, also with about this value, will lose some of its effectiveness and the chance of running into a dispersion region will be minimized. On the other hand, if GR-S is vulcanized to the same degree, its gel modulus, around 10^7 dynes/cm.² will dominate in one frequency range and the permanent network in another. This situation could, perhaps, be avoided by

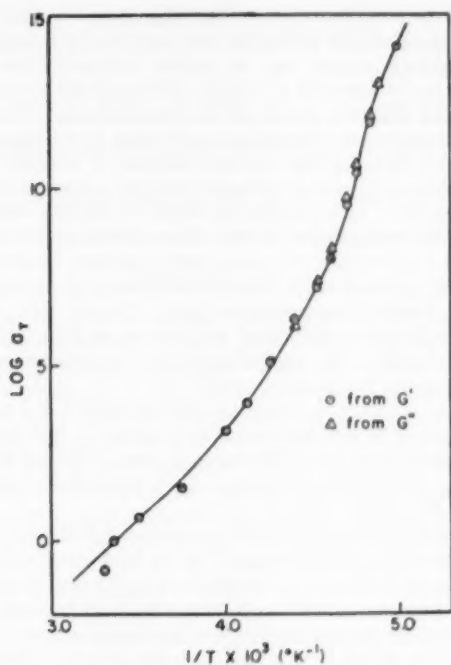


Fig. 9.—Plot of $\log a_T$ vs. $1/T$ for GR-S.

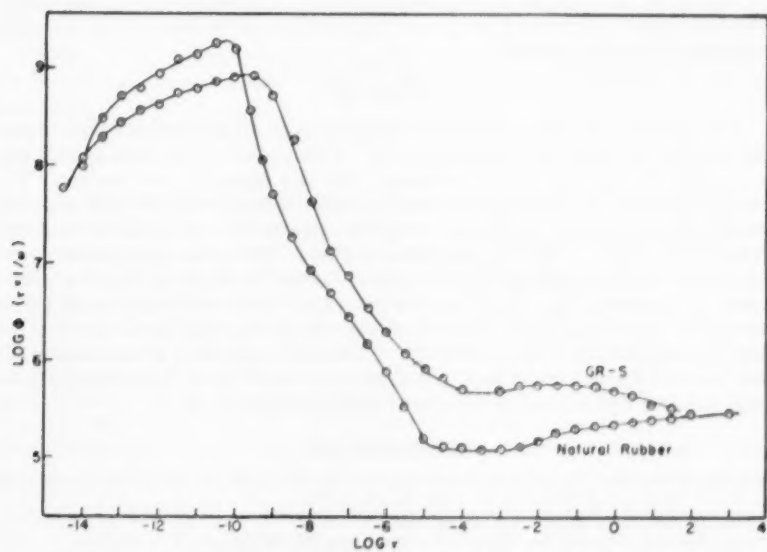


Fig. 10.—Distribution functions for GR-S and natural rubber.

vulcanizing GR-S to a higher degree, but this might adversely affect other properties, and, indeed, might defeat its own purpose by bringing the apparent second-order transition region up to higher temperatures. Dilution (oil extension) might also be expected to help by cutting down the number of chains per unit volume and thus the value of the gel modulus. In this connection, it must be remembered that oil extension will also lower the equilibrium vulcanized modulus, by virtue of the reduced number of effective chains per unit volume, if vulcanization is carried out so as to involve a given fraction of monomer units in cross-links. In this case, the whole modulus level will be lowered, probably without the elimination of any dispersion region. In order to compensate for this, a higher level of vulcanization should be sought so that the number of effective (permanently cross-linked) chains is increased by having a smaller molecular weight between cross-links. In this way, it is possible to insure that the equilibrium vulcanized modulus is as high as the gel modulus and any dispersion between the two eliminated. In what way the presence of fillers modifies the above behavior is not known.

There was some evidence in the present work that $\tan \delta$ and G'' might be starting to rise again after the limiting glassy modulus had been reached, and this suggests that there may be additional processes occurring at lower temperatures, that give rise to other loss peaks. Such peaks have been observed for other polymers in the glassy region⁶.

Some caution should be exercised in assigning significance to the absolute values of the reduced frequencies assigned to the transition regions of the superposed plots in Figures 5, 6, and 7. Aside from any possible inadequacy in the reduced variables treatment, such as might arise if all relaxation times do not depend the same way on temperature, there is considerable error possible in the shifting procedure, on which the values of a_T are based. Since the individual curve sections are shifted successively to coincidence, starting with that at room temperature, errors are cumulative. They are particularly severe in the flat region at the foot of the transition region. Uncertainties of one-half or even one decade in reduced frequency may easily accumulate by the time the transition region is reached.

SYNOPSIS

The dynamic moduli and loss factors have been determined for high-molecular samples of GR-S and natural rubber. Comparison of the two sets of data shows that the general characteristics of the two materials are similar. The main differences are that GR-S shows a higher temperature for the apparent second-order transition, and also a higher value for the modulus in the relatively level portion of the highly elastic region. The usual superposition procedures are used for correlating the data. Several indications that the equivalence of frequency and temperature may not be of universal applicability are noted. It is suggested that the higher elastic plateau modulus of GR-S may, in conjunction with usual levels of vulcanization, lead to a modulus dispersion, with its attendant loss, and thus be a contributing factor to the lower resilience and higher heat development characteristic of GR-S.

REFERENCES

- ¹ Tobolsky, *J. Am. Chem. Soc.* **74**, 3786 (1952); Tobolsky and McLoughlin, *J. Polymer Sci.* **8**, 543 (1952).
- ² Morrison, Zapas, and DeWitt, *Rev. Sci. Instr.* **26**, 357 (1955).
- ³ Ferry, Grandine, and Fitzgerald, *J. Applied Phys.* **24**, 911 (1953).
- ⁴ Witte and Anthony, *J. Applied Phys.* **22**, 689 (1951).
- ⁵ Ferry, Fitzgerald, Grandine, and Williams, *Ind. Eng. Chem.* **44**, 703 (1952).
- ⁶ Heyboer, Dekking, and Staverman, *Proceedings of the 2nd International Conference of Rheology*, Academic Press, New York, 1954, p. 123.

CHEMICAL RELAXATION OF STRESS IN POLYURETHAN ELASTOMERS *

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INTRODUCTION

In a recent series of communications from the Bayer Laboratories¹, the preparation and properties of a new series of polyurethan elastomers obtained from polyesters and diisocyanates have been described. These elastomers, under the generic term of Vulcollan, are analogous with the product known as Adiprene B, which has very recently been announced by the du Pont laboratories². This latter material differs chemically from Vulcollan in that the main network chain is composed of polyether segments rather than polyester segments. All these synthetic elastomers have been found to display excellent properties with respect to tear strength, tensile strength, abrasion resistance, rebound resilience, resistance to swelling in common organic solvents, and resistance to aging, deterioration from exposure to air or ozone. However, noticeable deleterious effects of temperature on elastic modulus and tensile strength were noted³, indicating that chemical changes were occurring.

The applicability of measurement of relaxation of stress at constant strain has been found useful in following the chemical network degradation of many polymeric substances, e.g., natural rubber, in which oxidative scission of chains was the prime factor⁴, and disulfide rubbers⁵, and silicone elastomers⁶, in which mutual exchange of network bonds was thought to be responsible for decay of stress.

The basic link between the mechanical behavior of a cross-linked polymer and its chemical constitution is given by the fundamental equation of rubber elasticity⁷:

$$f = NkT \left(\alpha - \frac{1}{\alpha^2} \right) \quad (1)$$

where f is the stress based on original cross-section, N is the number of network chains per unit volume of rubber, and α is the strain or relative elongation. At constant strain and temperature, the stress at any time should be proportional to the number of network chains maintaining stress per unit volume. Even if there were departure from this theory, it would be expected that a decay of stress would still be related to a decrease of the number of network chains maintaining stress. Since a dynamic equilibrium between breaking of bonds and reformation of new bonds is possible, "intermittent" measurements are made, in which the sample is stretched only for a period of time necessary to determine the stress, and then is released to its initial position. The latter measurement is believed to represent the difference between the rate of scission of bonds and the rate of formation of new bonds, whereas a continuous measure-

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ment of decay of stress is thought to measure only the decay of bonds, since any new bonds formed would be in equilibrium with the strained condition and not contribute to the stress⁸.

EXPERIMENTAL

MATERIALS

Samples of Vulcollans, prepared essentially as in patents and publications of the Bayer Company, were obtained from the United States Rubber Company, and used without any further treatment. Three basic types of compounds were investigated. Common to all three was the starting material, a polyester of molecular weight approximately 2000, prepared from adipic acid and a mixture of ethylene and propylene glycols. The components of the three samples were as follows:

- A. Polyester, diphenylmethane diisocyanate, and water as cross-linking agent.
- B. Polyester, naphthalene 1,5-diisocyanate, and 1,4-butanediol as cross-linking agent.
- C. Polyester, toluene 2,4-diisocyanate, and an aromatic diamine as cross-linking agent.

A sample of Adiprene B was kindly furnished by the du Pont laboratories.

EQUIPMENT AND PROCEDURE

All measurements were made on an instrument previously described⁴, except that the relaxometer was modified for use of strip samples. This proved very advantageous and convenient for these studies. A full description of this modification is given elsewhere⁹.

RESULTS AND DISCUSSION

Stress relaxation behavior of the three Vulcollans and Adiprene B have been studied over a temperature range of 90° to 130° C, and an extension of 20 per cent. Extension was not included as a variable, since it was shown to have little or no effect in other polymeric systems exhibiting stress decay due to cleavage of chemical bonds.

Our data have been presented in terms of percentage of residual stress, $100f/f_0$, as a function of logarithmic time. The original stress present in the sample was determined by graphical extrapolation to an arbitrary time, 0.01 hour in the case of continuous measurement, and 0.1 hour for intermittent measurements.

Absolute magnitudes of the initial modulus were reproducible within 5 per cent or better and duplicate determinations plotted on a relative basis were completely superposable. The data for the continuous runs for Vulcollan A are presented in Figure 1, and the intermittent data for Adiprene B in Figure 2. Comparison of stress decay curves for all samples at 120° C is made in Figure 3. Common to all four samples is the fact that all appear to approach zero stress asymptotically and that the greater portion of the decay takes place within two cycles of logarithmic time. Such behavior is similar to that shown by polysulfide rubber⁸, natural rubber⁸, and silicone rubber¹⁰. In these materials, chemical scission of bonds was deduced to be the underlying factor. None of

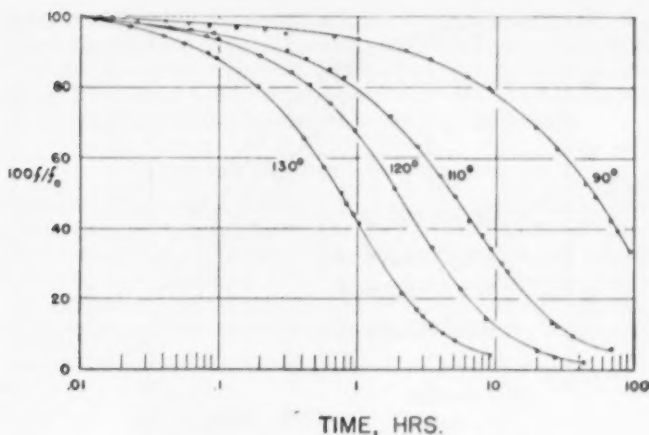


FIG. 1.—Continuous stress relaxation of Vulcollan A.

the linear polymers which stress-relax owing to internal flow processes have ever shown a two-cycle decay, but extend over many cycles of logarithmic time. Of course, predominantly chemical relaxation effects would be expected in an extended three-dimensional structure such as polyurethan rubber, in which flow would be ruled out as a rate-controlling step.

For natural rubber and polysulfides at high temperatures, a good fit was found to the equation $f/f_0 = e^{-t/\tau}$, in which τ is a characteristic relaxation time, and this also approximately fits the chemical stress decay of polyurethan rubbers. The magnitude of τ may be calculated as the reciprocal of the time required for the force to reach $1/e$ of its initial value. By identification of $1/\tau$ with a chemical rate constant k , it is then possible to determine an activation energy for the process. A composite plot of $-\log \tau$ or $\log k$ vs. $1/T$ is given in

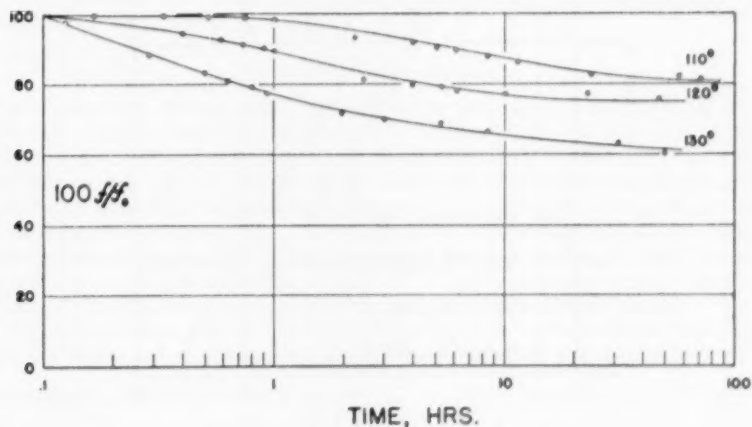


FIG. 2.—Intermittent relaxation of Adiprene B.

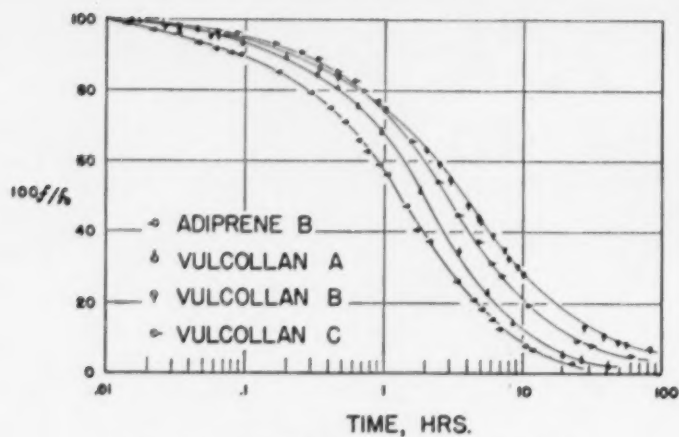


Fig. 3.—Continuous stress-relaxation of polyurethanes at 120° C.

Figure 4. Activation energies were computed from the slopes in the usual way, and are summarized in Table I. It is seen that all have the same order of magnitude, and the sample which shows the most rapid stress decay (Adiprene B) relaxes only about 2.5 times as fast as the Vulcollan B, which is the slowest.

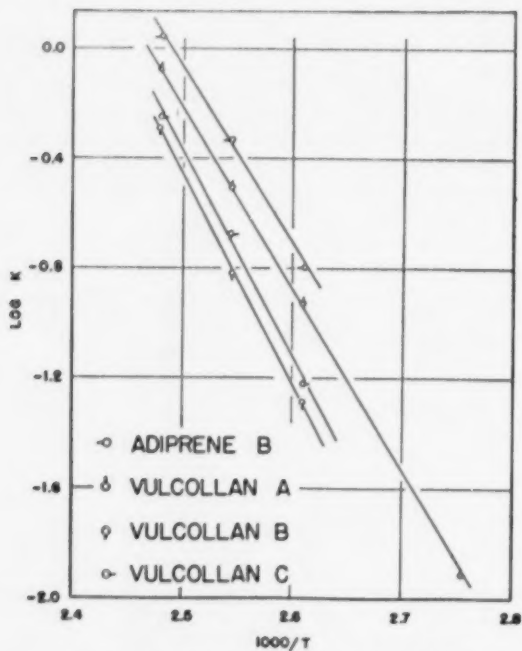


Fig. 4.—Temperature dependence of relaxation times.

Referring to Figure 2, the results of the intermittent runs are in marked contrast to the continuous stress relaxation. The intermittent curves for Vulcollan C are similar to this. Since the decay of stress here is due to the difference between the rate of bond formation and the rate of bond cleavage, it is apparent that considerable reformation of bonds is taking place.

EFFECTS OF ADDED SUBSTANCES

Preliminary experiments were begun to determine the effects of extraneous chemical substances introduced into the rubber. Vulcollan A was immersed in water at 90° C for 1 hour, with weight increase of 2 per cent, and then its stress decay characteristics determined at 90° C in an atmosphere containing water vapor. No difference between treated and untreated polymer was discernible in either the continuous or intermittent relaxation curves. To determine the

TABLE I

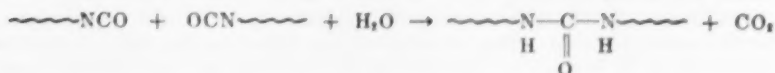
Sample	Activation energy
Vulcollan A	29.9 ± 2
Vulcollan B	35 ± 1
Vulcollan C	34 ± 3
Adiprene B	30.5 ± 0.5

effect of incorporated hydroxyl groups, a compound was sought in which a high degree of weight retention was available at elevated temperatures. A specimen of Vulcollan B was immersed in polyethylene glycol No. 300 at 80° C for 1 hour. There resulted an initial weight increase of 16 per cent, and at the end of 40 hours in a circulating oven at 110° C, about half of this quantity was still present in the rubber. A marked physical change had also appeared, in that the rubber became very soft and possessed very low tear strength. More quantitative information is provided by the comparison of the continuous stress relaxation curves for both the untreated sample and the one in which polyethylene glycol was present. For the untreated sample at 110° C, the time to attain 1/e of the initial retractive force is 19 hours, contrasted with 6.8 hours for the treated sample. The mechanism for this reaction is not yet known; the glycol groups could presumably exchange with the main-chain polyester linkages or possibly with the urethan linkages.

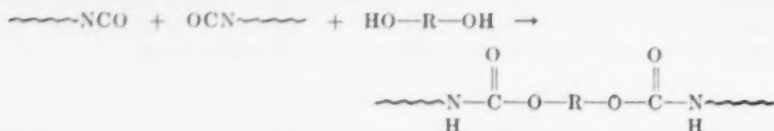
STRUCTURE OF POLYMERS

A brief review of the general methods of preparation of these polymers will reveal the labile points at which network scission might be expected. The basic process may be divided into chain formation, chain lengthening, and network formation. Common to all three Vulcollans was the starting material of polyester of molecular weight 2000, prepared from adipic acid and a mixture of ethylene and propylene glycols. By addition of a 30 per cent excess of a diisocyanate, generally aromatic, it was possible to link two or three of these chains together by formation of urethan bonds. Further lengthening of the chains is possible through the following processes, outlined by the Bayer papers:

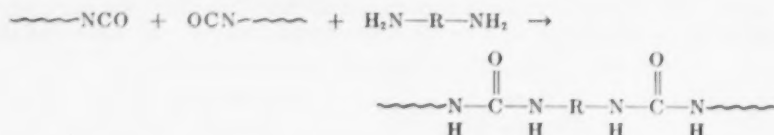
A). Addition of water will cause the elimination of carbon dioxide between two isocyanate groups through formation of a substituted urea bridge, thus:



B). Addition of a glycol proceeds by linking two polyester chains through formation of adjacent urethan groups, thus:



C). Addition of a diamine leads again to the coupling of two polyester chains through adjacent urea groups, thus:



Cross-linking in the case of (A) and (C) is thought to proceed via reaction of the hydrogen atoms in the newly formed urea groups with isocyanate polyester chains still present. Analogous reactions of low molecular-weight disubstituted ureas have been found to proceed in this manner, through formation of new urea linkages, giving a substituted biuret structure. In like manner it is reasonable to assume that the hydrogen atoms in the newly formed urethan groups of (B) furnish the sites for cross-linking. Lower molecular-weight analogs of this reaction are likewise known. In the elastomer formation, however, it is at present not known whether one or both of the urethan hydrogens are capable of further reaction.

Complete information regarding the formation and structure of Adiprene B is not at present available, although it is known that the main network chains are formed from polyethers rather than polyesters, and the chain lengthening process also proceeds via formation of urethan bonds.

POSSIBILITIES FOR BOND SCISSION

1. *Ester cleavage.*—Referring again to the experimental stress relaxation data, it seems reasonable to rule out the possibility of stress decay by virtue of ester-ester interchange, since parallel behavior is shown by the polyether urethan as well. In addition, previous experiments in this laboratory¹¹ show that a much slower chemical decay of stress is present in elastomeric polyester vulcanizates of both the Paraplex type and the similar polyester rubbers of the succinic acid-propylene glycol type (vulcanized by benzoyl peroxide) which were originated in the Bell Telephone Laboratories. For example, in a continuous stress relaxation experiment at 130° C, the time required to reach 1/e of the initial value of the modulus was 75 hours for the Bell Telephone rubber. These times varied from 34 hours to 240 hours for the Paraplex series. On the other hand, for the Vulcollan type rubbers, the relaxation times were approximately 1 hour at 130° C.

2. *Urethan cleavage.*—Simple low molecular-weight urethans are known to be thermally unstable. The presence of the corresponding isocyanates has been noted by Hofmann¹² on distillation of phenyl, tolyl, and naphthyl urethans.

An extensive investigation has been made by Petersen and others¹² on decomposition products of urethans formed from low molecular-weight diisocyanates. By use of their Cellit (acetylcellulose) test, it was possible to define a characteristic decomposition temperature for each urethan. For many of these compounds characteristic temperatures of 180° C were found, although a few extended as low as 120°–130°C. It is, therefore, not impossible that urethan cleavages in the elastomer are responsible for the observed stress decay.

3. *Disubstituted ureas*.—Simple low molecular-weight disubstituted ureas are also known to be thermally unstable. Utilization of the thermal decomposition of substituted ureas has led to the synthesis of isocyanates by vaporization of ureas in the presence of hydrogen chloride¹⁴, although a temperature of 370° C was required for 99 per cent dissociation. Qualitatively the presence of isocyanates has been observed in liquid phase decomposition of ureas¹⁵, in solution¹⁶, and by distillation of molten disubstituted ureas¹⁷, and treatment of molten ureas with phosphoric anhydride¹⁸ or dry hydrogen chloride¹⁸. The difficulty of applying this decomposition as a synthetic method lies in the recombination of products. This recombination appears relevant to the interpretation of our intermittent stress curves, which measure the net change between bonds cleaved and bonds reformed.

In many cases the cross-links are very probably trisubstituted urea linkages. These would also be a possible site for bond scission, and we feel instinctively that this is a very likely possibility.

4. *Urethan vs. substituted urea linkages as the labile sites*.—It has not been possible, with the data at hand, to ascertain more definitely the actual site of network scission.

If scission were to occur at cross-links only, the relaxation time at a given temperature would be independent of the modulus of the specimen, i.e., independent of the concentration of cross-linkages. If the scission occurs at urethan linkages between cross-links, then the relaxation time would be inversely proportional to the number of urethan linkages between cross-links, i.e., it would be shorter for specimens of low modulus. For certain rubbers, the substituted urea linkages might occur only at the cross-links.

A possible clue as to which bonds are being attacked might be obtained by studying rubbers prepared from polyesters of different degrees of polymerization.

SUMMARY

The chemical stress-behavior of polyester urethan elastomers and a polyether elastomer have been determined through a temperature range of 90° to 130° C. Since both the polyether and polyester had approximately the same rates of stress decay, it was necessary to exclude ester-ester interchange as a reaction mechanism, and to regard the known thermal lability of the urea and urethan groups as indicative of possible sites of network scission. A likely possibility for the weak link is the trisubstituted urea (biuret) cross-linkage.

REFERENCES

- ¹ Bayer, *Ann.* **549**, 286 (1941); *Angew. Chem.* **59**, 257 (1947); Hebermehl, *Farben, Lacke, u. Anstrichstoffe* **8**, 123 (1948); Siefken, *Ann.* **562**, 75 (1949); Petersen, *Ann.* **562**, 205 (1949); Bayer, Müller, Petersen, Piepenbrink, and Windemuth, *Angew. Chem.* **62**, 57 (1950); *RUBBER CHEM. & TECHNOL.* **23**, 812 (1950); Hechtlen, *Kunststoffe* **40**, 221 (1950); Müller, Bayer, Petersen, Piepenbrink, Schmidt, and Weinbrenner, *Angew. Chem.* **64**, 523 (1952); *RUBBER CHEM. & TECHNOL.* **25**, 493 (1953).
- ² Hill, Young, Nelson, and Arnold, paper presented at the Detroit meeting of the Division of Rubber Chemistry of the American Chemical Society, May 4–6, 1955. Reported in *Chem. Eng. News* **33**, 2079 (1955).

- ¹ Bayer, Muller, Peterson, Piepenbrink, and Windenmuth, *Angew. Chem.* **62**, 57 (1950); *RUBBER CHEM. & Technol.* **23**, 812 (1950).
- ² Tobolsky, Prettyman, and Dillon, *J. Applied Physics* **15**, 380 (1944).
- ³ Stern and Tobolsky, *J. Chem. Physics* **14**, 93 (1946); Mochulsky and Tobolsky, *Ind. Eng. Chem.* **40**, 2155 (1948).
- ⁴ Johnson, McLoughlin, and Tobolsky, *J. Phys. Chem.* **58**, 1073 (1954); Outhoff, Busche, and Grubb, *J. Am. Chem. Soc.* **76**, 4659 (1954).
- ⁵ Siefken, *Ann.* **562**, 75 (1949).
- ⁶ Tobolsky, Prettyman, and Dillon, *J. Applied Physics* **15**, 380 (1944); Mark and Tobolsky, "Physical Chemistry of High Polymeric Systems", Interscience Publishers, Inc., New York, 1950, p. 330.
- ⁷ Offenbach, J. A., Ph.D. Thesis, Princeton Univ.
- ⁸ Johnson, McLoughlin, and Tobolsky, *J. Phys. Chem.* **58**, 1073 (1954).
- ⁹ Andrews, R. D., Ph.D. Thesis, Princeton University, 1948.
- ¹⁰ Hofmann, *Ber.* **3**, 653 (1870).
- ¹¹ Peterson, *Ann.* **562**, 205 (1949).
- ¹² Bennett, Saunders, and Hardy, *J. Am. Chem. Soc.* **75**, 2101 (1953).
- ¹³ Eckenroth and Wolf, *Ber.* **26**, 1463 (1893).
- ¹⁴ Iwakura and Nakakubo, *Bull. Tokyo Inst. Technol.* **13**, 25 (1948).
- ¹⁵ Hofmann, *Ber.* **14**, 2725 (1881).
- ¹⁶ Habich and Limpricht, *Ann.* **109**, 101 (1859).

THE PHOTOELASTIC EXAMINATION OF RUBBER ARTICLES *

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GENERAL CONSIDERATIONS

As is known, it is possible to calculate the distribution of internal stresses in a solid body which is subjected to mechanical action by making use of a suitable transparent model stressed in a similar way and by examining the model in polarized light between crossed nicol prisms.

When the solid to be examined is planar and subjected to a system of forces which all act in the same plane, the photoelastic method can be applied quite simply. When a ray of polarized light passes through the model, the light itself is changed by accidental birefringence resulting from the material being in a state of strain. The ray of light, analyzed as it emerges from the model, takes the form of illuminated zones and dark zones, from which both the intensity and the direction of the internal stresses can be determined.

When the solid to be examined is not planar, it is necessary to have recourse to special techniques of three-dimensional photoelasticity. By this means, tests are still possible, but difficulties are encountered both in the preparation of models and also in their optical examination and in the interpretation of the results obtained.

Although examination of three-dimensional stresses in solid rubber objects which are highly deformed is possible experimentally, in the majority of cases an examination of plane models can, even if it gives only approximate results, be regarded as satisfactory, and therefore all the considerations in the present report are limited to this particular case.

Before passing on to a brief description of the photoelastic method, some accepted definitions of terms concerned with the subject under discussion may be given.

Principal directions.—These are the three spatial directions, perpendicular to each other, along which the stress at every point is a normal one. In a plane, there are two principal directions, and the normal stress along each of them is a maximum or a minimum with respect to those which act in the other directions.

Principal stresses.—These are the normal stresses which act along the principal directions.

Principal strains.—These are the strains corresponding to the principal stresses in an isotropic material.

Stress trajectories.—These are lines whose tangents are every point on them coincide with one of the principal directions at the same point.

ACCIDENTAL BIREFRINGENCE

A ray of monochromatic polarized light which passes through a sheet of transparent isotropic material perpendicular to its plane is decomposed, when

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the sheet is stressed, into two rays vibrating in planes perpendicular to each other, whose paths in the sheet coincide with the principal directions.

The two emerging rays are out of phase by the angle:

$$\varphi = \frac{2\pi C_1 e(p - q)}{\lambda} \quad (1)$$

where C_1 is the photoelastic coefficient characteristic of the particular material which can be determined experimentally; e is the thickness of the sheet being studied; $p - q$ is the difference between the principal stresses; and λ is the wave length of the particular light used.

The two rays of light return into phase on emerging from the model when

$$\varphi = 2K\pi, \text{ i.e., } p - q = \frac{K\lambda}{C_1 e} \quad (2)$$

where K is a whole number which may have the values $1, 2, \dots, n$.

At those points where Equation (2) holds true, the polarized light is reconstituted in the same plane of the incident ray, which is then extinguished by the analyzer.

The geometric position of the points, where, for a given value of K , Equation (2) is valid, is a dark line or fringe which may be called isochromatic. Within its limits the difference between the principal stresses is constant.

To each K value there is a corresponding fringe, and K defines its order. The lines of increasing order, $1, 2, \dots, n$, correspond to differences between the principal stresses which are multiples of each other. It is possible by various methods to pass from the differences to the magnitude of the principal stresses¹.

Operating with white light instead of with monochromatic light, colored lines instead of dark lines appear. Since white light has a continuous spectrum of wave lengths, all radiation of wave length:

$$\lambda = \frac{C_1 e(p - q)}{K} \quad (3)$$

will be extinguished at every point.

The fringes appear, therefore, in the complementary colors of the extinguished wave lengths. It may happen that one of the principal directions at some point in the sheet of material being examined coincides with the plane of polarization of the incident ray of light. This latter is then not decomposed, but is extinguished by the analyzer. The location of the points where one of the principal directions is parallel to the plane of polarization of the incident ray of light is termed the *isoclinic* line or zone. Such lines vary in position according to the angle formed by the plane of polarization of the incident light ray with a reference plane. From the isoclinic, it is possible to derive the stress trajectories by simple geometric construction.

APPLICATIONS OF THE METHOD TO THE EXAMINATION OF HIGH DEFORMATIONS OF RUBBER ARTICLES

When the question is one of examining highly deformable rubber articles, it is necessary to utilize models which are highly deformable themselves. Any examination of a thin model which represents the section of a solid subjected to mechanical stress is a problem in which special conditions are involved because

of the high deformability of the solid. If the model is subjected to tension, it remains planar, but its thickness decreases from point to point in a way which depends on the loading system applied and on the external profile. In this case, examination is still possible, but the results obtained are only qualitative.

If the model is subjected to compression, there is lateral flexure because the model is so thin (which is necessary to obtain satisfactory transparency) or else its thickness increases. To avoid any increase of thickness, and particularly to avoid lateral flexure of compressed models, it was decided to place them between parallel glass plates whose inner walls are located at a distance equal to the thickness of the models and are held rigid by a strong metal frame (see Figure 1).

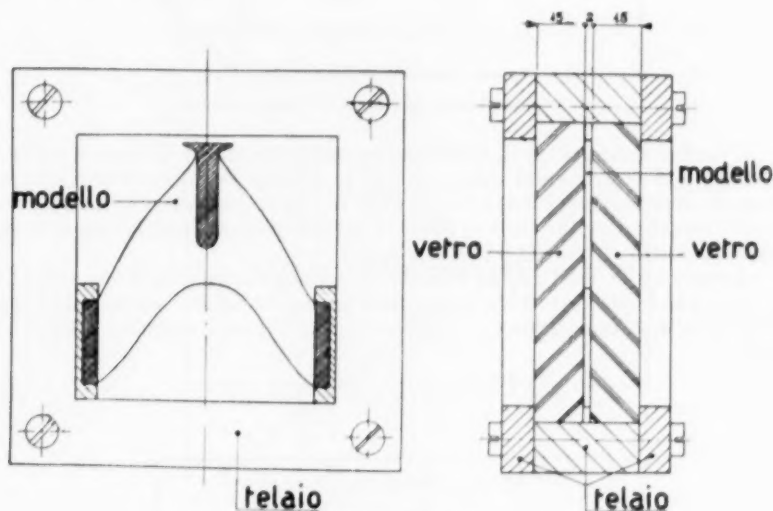


Fig. 1.—Method for studying thin models of rubber. Location of the model between glass plates.

The inner walls of the glass plates should be lubricated with castor oil or glycerol so as to eliminate any tangential tensions, due to friction, in the loaded model.

Observations made in this way of rubber models differ considerably from observations of models constructed of materials which are relatively only slightly deformable and which are placed free between the polarizer and analyzer. Actually in this second case it is possible, as has been mentioned, to derive directly, from the order of the fringes, the differences of the principal stresses ($p - q$) acting in the plane of the model, to which correspond the strains ϵ_p and ϵ_q coplanar with p and q , and ϵ_r perpendicular to the first two. The stress, r , perpendicular both to p and to q , is zero, because the model is stressed, as has been said, only by forces acting in the same plane.

In the case of highly deformed rubber models, located between glass plates and subjected to compressive forces acting on its plane, a stress r is set up against the plates themselves, to which corresponds a strain ϵ_r equal to zero.

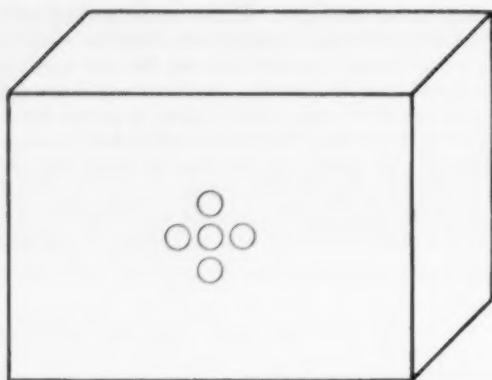


Fig. 2.—Test-specimen used for standardizing materials.

A further examination is, therefore, necessary by means of theoretical deductions and experimental measurements to be able to interpret the fringes from the observations of the model; in other words, it is necessary to know what value characterizing the state of strain of the model is proportional to, or is at least a function of, the order of the fringes.

A study by Treloar² dealing with the electrical polarizability of long molecular chains and the effect on the propagation of electromagnetic waves, led to the conclusion that, in addition to Equation (1), the following equation likewise is valid:

$$\varphi = \frac{2\pi C_7 e}{\lambda} [(1 + \epsilon_p)^2 - (1 + \epsilon_q)^2] \quad (4)$$

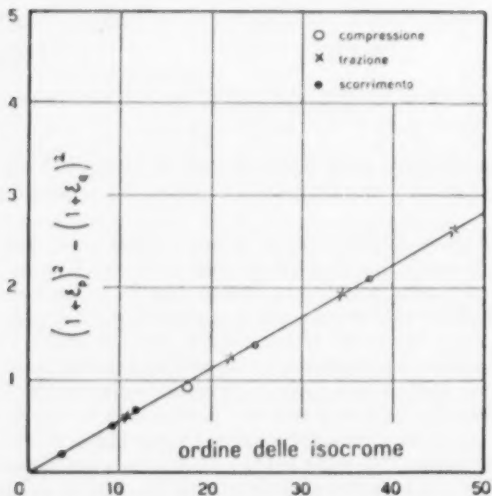


Fig. 3.—Verification of the relation indicated by Treloar.

Equation (4) resolves itself into Equation (1) if account is taken of the fact that, in the case of rubber, and again according to Treloar:

$$p - q = NKT[(1 + \epsilon_p)^2 - (1 + \epsilon_q)^2] \quad (5)$$

where K is the Boltzmann constant, T is the absolute temperature, and N is the number of molecular chains per unit volume.

Since Equation (4) has been derived on a theoretical basis, we have chosen to verify it experimentally. To this end, prismatic models of transparent rubber of different dimensions were prepared, and were then subjected to compression, tension, and shearing, without placing them between glass plates, but leaving them free to increase in thickness when compressed, to become thinner when stretched, and to maintain a constant thickness when sheared.

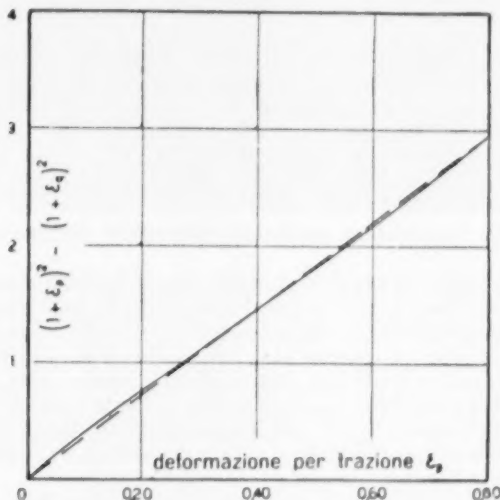


Fig. 4.—Relation between the factors ϵ_p and $[(1 + \epsilon_p)^2 - (1 + \epsilon_q)^2]$ for simple shearing. The solid line represents the exact relation; the broken line represents the approximate linear relation.

In the case of rubber, the stresses are not distributed uniformly in the interior of the models except for very small deformations far removed from those usually met with in ordinary service, but rather only under unusual service conditions. To eliminate this drawback, there were imprinted, directly by vulcanization, on the central part of one of the external faces of the models to be studied, a few small rings, of 3 mm. diameter, and with extremely thin profile (see Figure 2). When these models were placed between crossed-nicol prisms, it was possible to measure microscopically the axes of the ellipses formed by each deformed ring, and thus to determine at one time the fringe passing through the ring itself, which in the cases described largely covered the ring.

The ratio between the major or minor axis of the ellipse and the diameter of the ring gives the values of $1 + \epsilon_p$ and $1 + \epsilon_q$, respectively.

The results which were obtained are shown diagrammatically in Figure 3 and help to verify Equation (4). Naturally this diagram has been corrected in the case of tension and also in the case of compression because of variations

in the thickness of the model and, in its final form, it is based on a thickness of 1 cm. for the model itself.

In the case of shear, which is obtained in the absolute sense only under special experimental conditions, which in the present work were approximated to the greatest degree possible, the thickness of the model does not change, i.e., $\epsilon_z = 0$. If account is taken of the fact that the volume of the rubber remains practically unchanged during deformation, the relation between ϵ_p and ϵ_q is in such a case:

$$1 + \epsilon_q = \frac{1}{1 + \epsilon_p} \quad (6)$$

so that:

$$(1 + \epsilon_p)^2 - (1 + \epsilon_q)^2 = (1 + \epsilon_p)^2 - \left(\frac{1}{1 + \epsilon_p} \right)^2 \quad (7)$$

The second member of Equation (7) is, accordingly, practically a linear function of ϵ_p , at least when $\epsilon_p < 0.80$, as can be seen in the diagram (Figure 4).

This means that, in the case of shear, Equation (4) can be written thus:

$$\varphi \cong \frac{2\pi c_2 e}{\lambda} \cdot \epsilon_p \quad (8)$$

This equation has also been verified experimentally, and is valid within the limits cited.

If now we consider the problem of models placed between glass plates in the way already described, it will be found that, in these conditions too, $\epsilon_z = 0$ (except for points pertaining to the boundary of the model, when along which a tension stress trajectory is tangent); i.e., the various points of the model are in a state of deformation similar to that existing in shear. The correctness of Equation (8) was established experimentally, and was found to be valid also for these last conditions. In this way it is demonstrated that the birefringence of rubber depends only on the state of deformation existing at each point of the particular model under examination.

The relatively simple relation represented by Equation (8) makes easy the examination of models, even if such a method leads only to the estimation of the principal strains and not of the stresses involved.

EXPERIMENTAL PROCEDURE

The equipment and materials normally used include two polaroid plates of about 20 cm. diameter placed at a distance varying from 15 to 20 cm. parallel and coaxial. Their arrangement is such that a ray of light leaving the first polarizer is extinguished by the second polarizer.

The illumination may be white light or monochromatic light, e.g., that from a sodium-vapor lamp. A translucent glass is placed between the source of light and the first polarizer (see Figure 5).

A rubber mixture used in many cases for preparing the models has the following composition: first-latex crepe 100, sulfur 1, tetramethylthiuram monosulfide 0.35, diphenylguanidine 0.5, stearic acid 0.5, and zinc oxide 1 part. This is vulcanized 50 minutes at 122° C.

In testing a model, it is advisable to apply the loads gradually and to follow the formation of successive fringes and keep count of their order. In some cases

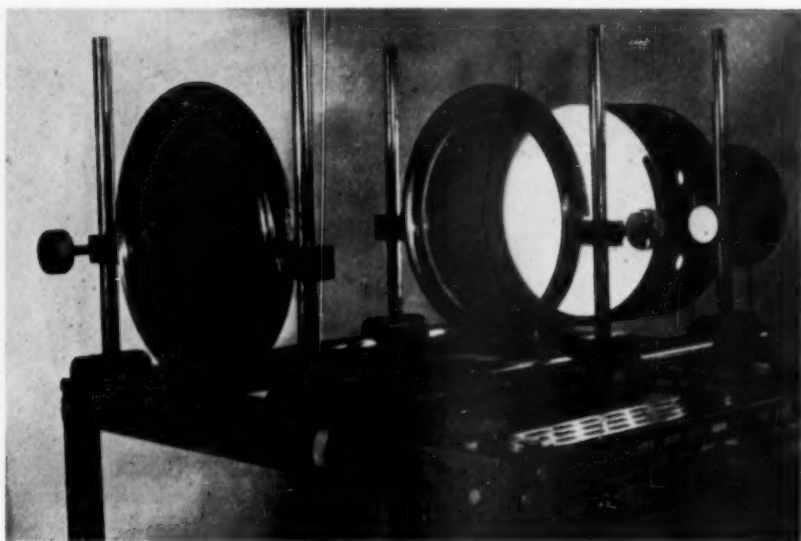


FIG. 5.—Apparatus for photoelastic examinations.

fringes of increasing or decreasing order are so numerous and so close together that a microscope is an indispensable means of counting them.

The isoclinics are likewise visible, particularly with models whose thickness is 2–3 mm. These can be eliminated by inserting between the polarizers, on the sides facing the model, two thin quarter-wave plates properly oriented. The same result is obtained in photography by rotating the polarizers by an angle of 90° during the exposure. In fact, while the isoclinics are related to the angle formed by the plane of polarization and a direction of origin, the fringes depend only on the difference in the optical path between the two rays emerging from the model. If the plane of polarization rotates rapidly in the time interval

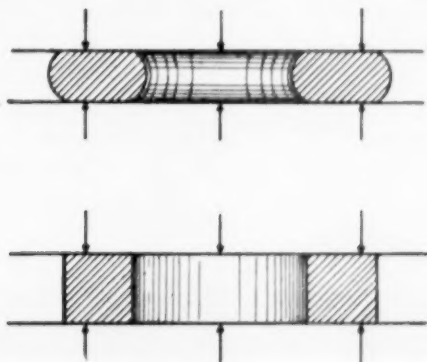
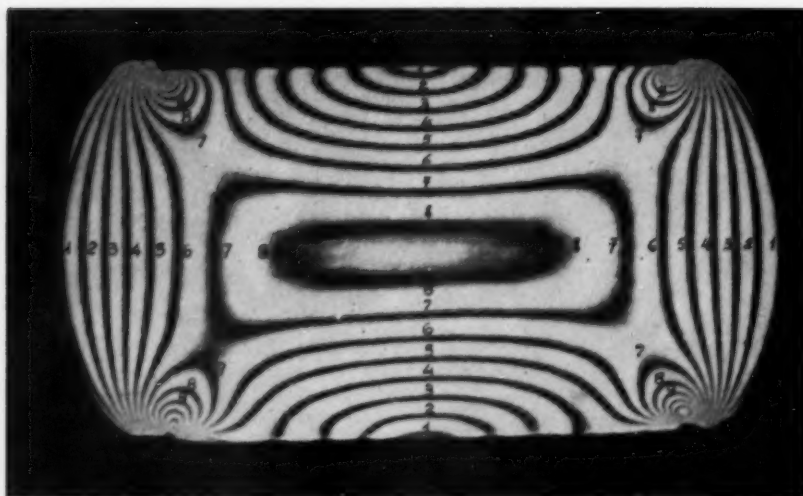


FIG. 6.—Ring having a square cross-section compressed between two planes.



[[Fig. 7.—Fringes of a model representing the section of the ring shown in Figure 6 and compressed 30 per cent.

(polarized light emerging circularly from the first quarter-wave plate), the isoclinics will no longer be visible, while the fringes will remain perfectly evident.

A practical example will serve to clarify some of the concepts which have been discussed. Let us imagine an annular ring of square cross-section compressed between two parallel plates (see Figure 6).

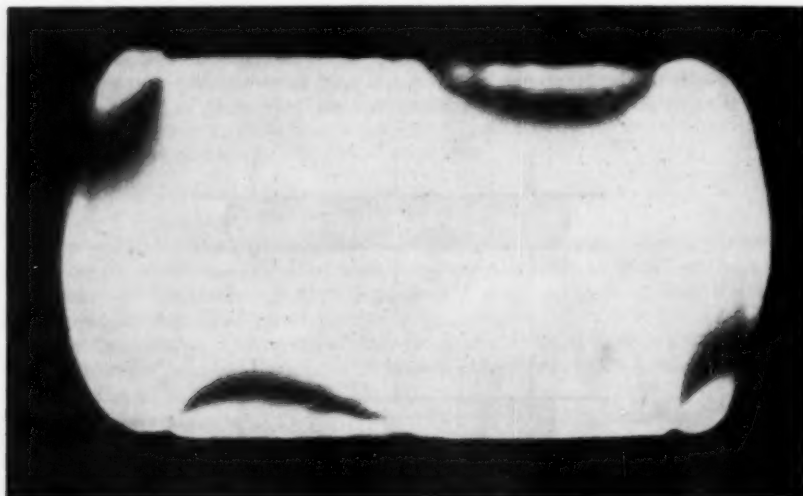


Fig. 8.—Isoclinics in the model of the section of the ring shown in Figure 6, compressed 30 per cent, when the plane of polarization of light is inclined 20° from the vertical.

If the mean diameter of the ring is sufficiently great with respect to the diameter of the cross-section, the latter can be regarded as pertaining to a prism with base of infinite length. If the distribution of the deformations is to be studied, a transparent model of the section having a thickness of a few millimeters is constructed. After having placed this model between glass plates, it is compressed in the same way as a section of the actual ring would be compressed.

In Figure 7 fringes are visible when the compression is 30 per cent, and in Figure 8 the isoclinics are visible for an angle of 20° between the vertical and the direction of polarization of the light which passes through the rubber model. In Figure 9 the stress trajectories drawn from the isoclinics are shown.

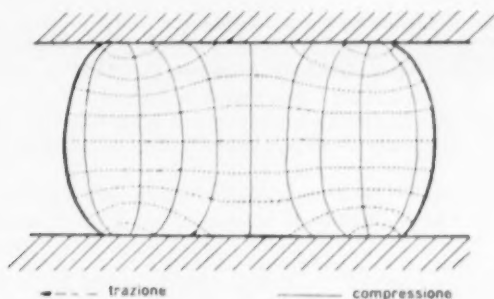


Fig. 9.—Stress trajectories in the section of the ring shown in Figure 6, compressed 30 per cent.

APPLICATIONS

The method makes possible the easy examination of various sections of solid rubber objects, and an exact picture is obtained of the state of deformation of any section when the deformation perpendicular to the section under consideration is zero. In all other cases the picture is more or less an approximate one.

The study of the deformation of rubber objects has proved to be of great utility because, as a result, the behavior of an article subjected to fatigue can be predicted. It has been found that rupture is essentially a surface phenomenon which takes place where a tension stress trajectory is tangent to an external boundary, and, with otherwise equal conditions, where the deformation is greatest².

The relative simplicity of application of this method therefore renders it of considerable value in the study of rubber articles designed for service where mechanical action is involved.

SUMMARY

After a short introduction to the photoelastic method and its applications to the examination of transparent planar structural models, some methods of examining plane models representing sections of actual rubber articles are indicated.

In many cases it is advisable to place the model between parallel glass plates with their inner faces lubricated and at a distance apart equal to the thickness

of the model itself. In other cases free models can be examined. In no case, however, is the law governing the birefringence of transparent materials within a range of small deformations, e.g., less than 1 per cent, equally applicable to greater deformations, e.g., up to 100 per cent. But in this range recourse can then be had to a law, based essentially on theoretical considerations and described by Treloar, which is an extension of the general law and which has been verified experimentally.

Some special cases are considered where the law is of general application to the quantitative evaluation of the state of deformation at various points in a model under examination.

REFERENCES

- ¹ Frocht, "Photoelasticity", John Wiley & Sons, Inc., New York.
- ² Treloar, "The Photoelastic Properties of Rubber", *Trans. Faraday Soc.* **43**, 277 (1947).
- ³ Angioletti, "Photoelastic Studies Concerned with Fatigue Phenomena in Rubber Articles", *Kautschuk u. Gummi* **6**, WT-171 (1953); *RUBBER CHEM. & TECHNOL.* **27**, 839 (1954).

ACCIDENTAL FACTORS INVOLVED IN THE FATIGUE BREAKDOWN OF RUBBER ARTICLES *

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GENERAL CONSIDERATIONS

In an earlier work¹ certain aspects of the process of the formation of cracks in vulcanized rubber articles subjected to repeated stresses were examined. This phenomenon is closely related to the state of elastic stress on the surfaces of the objects; in fact, a crack first forms at the zones on the free surface of the article which are strained most during fatigue stressing. Such a crack appears in the form of a fissure or cut oriented perpendicular to the direction of the tensile force.

On the other hand, the factors which can initiate fatigue cracking were not considered. These factors can in general be divided according to their origin into three groups:

(1) Factors which act in a chemical way on the surface of the article being stressed, e.g., oxygen, ozone, and other peroxides in the air. The literature on this subject is extensive².

(2) Factors of a physico-chemical character which are related to the structure of the material itself under stress and which depend on the number and type of bonds formed by vulcanization, on the length of the molecular chain between two links on the type of loading, and on the forces of adhesion of the granules to the surrounding rubber³.

(3) Factors of an accidental character, such, for example, as impurities in the rubber or in the compounding ingredients, poor dispersion of the fillers or vulcanizing agents, and, in general, almost any form of discontinuity in the vulcanized rubber caused by the presence of substances which have higher moduli and which are concentrated in a very restricted zone and thereby give rise to local stresses which are greater than those distributed in the surrounding medium. In this connection, attention is called to the discussion of Shepard, Street, and Park⁴, based on preceding published work.

All these factors are usually superposed, and the relative part played by each of them in determining the formation of cracks is not easily definable.

In the present study the purpose was to examine, first of all, the influence of accidental factors from the viewpoint of the stress concentration set up by a granule of a hard substance in the surrounding vulcanized rubber under stress. Obviously this case must be presented schematically.

In addition, an examination was made of the stress concentration inside an incision of the type of those which may be caused by ozone or by some of the accidental factors. Here too, a schematic presentation is necessary.

As a beginning, a study was made of these two cases because the investiga-

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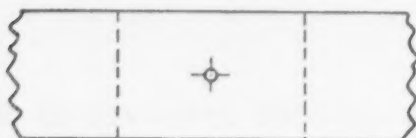


Fig. 1a



Fig. 1b

Figs. 1a and 1b.—Locations of metal disks inserted in strips of transparent vulcanized rubber.

tion could be carried out for the most part by means of the photoelastic method already described¹, and this was relatively simple.

EXPERIMENTAL METHOD

In applying the photoelastic method, it was necessary, as has already been mentioned, to simplify and outline the problem schematically. First of all, the scale of the linear dimensions was greatly increased so as to have granules and incisions which lend themselves to direct examination. It was assumed, however, that this does not lead to appreciable errors, as will be seen by a comparison of corresponding results on a different scale.

The actual shape of the granules and of the incisions varies greatly and is very irregular. A first simplification might be to substitute the granule by a sphere within the vulcanized rubber, but since the photoelastic method is practically limited to the solution of planar problems, it was necessary to simplify it further by examining in polarized light, and between crossed nicol prisms, small prismatic strips of transparent vulcanized rubber under strain and containing small metal disks of the same thickness (see Figure 1). As a result of these simplifications, results obtained with the photoelastic method are only qualitative.

In the case of an incision, it would have been interesting also to study the problem spatially by making an incision schematically on a more or less wide

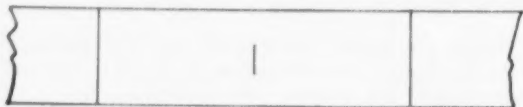


Fig. 2a

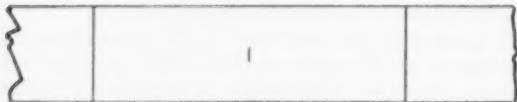
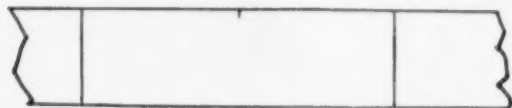


Fig. 2b

Figs. 2a and 2b.—Locations and dimensions of incisions at the center of strips of transparent vulcanized rubber.

Fig. 3^aFig. 3^b

FIGS. 3a and 3b.—Locations and dimensions of incisions on the edge of strips of transparent vulcanized rubber.

and deep cut made on one face of a prism of vulcanized rubber. The greatest concentration of stress, when the prism is strained, would certainly be in the deepest part of the incision and at its outer edges. Instead, the examination was limited to the planar case of a cut made in the center of a strip of transparent rubber or on one of the lateral edges of the strip (see Figures 2 and 3). In the second case, in addition to the photoelastic method, a simple approach to be discussed later was employed.

EXPERIMENTAL CONDITIONS

CHARACTERISTICS OF THE VULCANIZATE USED FOR THE TEST-SPECIMENS

The transparent mixture used was that normally chosen for examination in polarized light. The shear modulus G is approximately 3 kg. per sq. cm. In

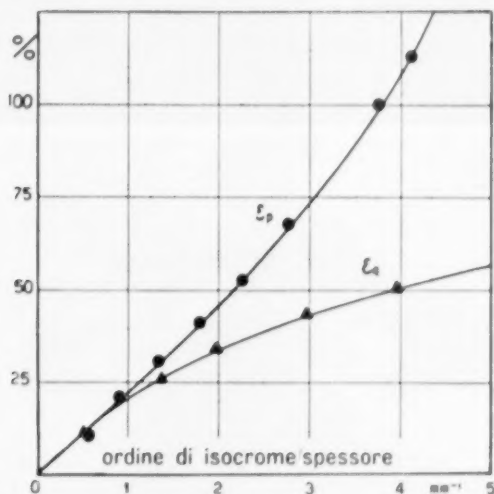
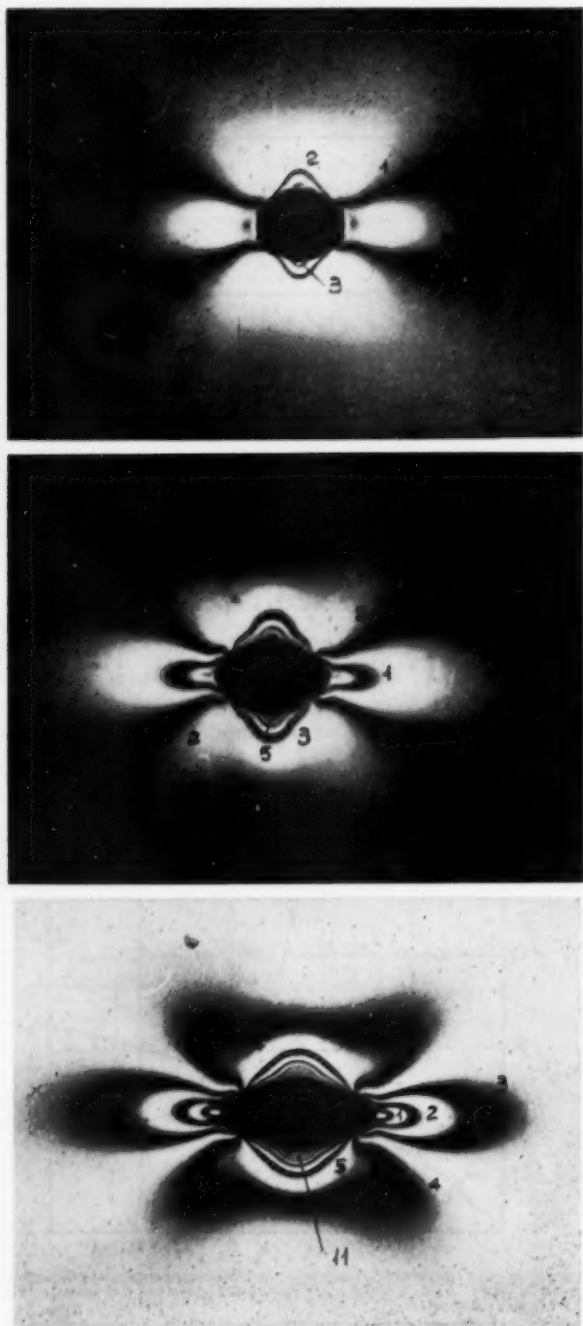
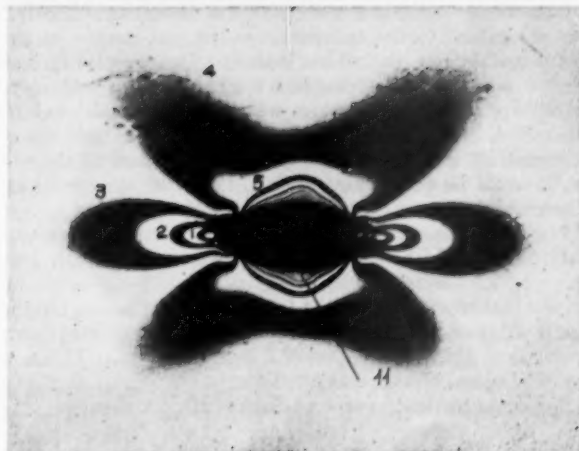
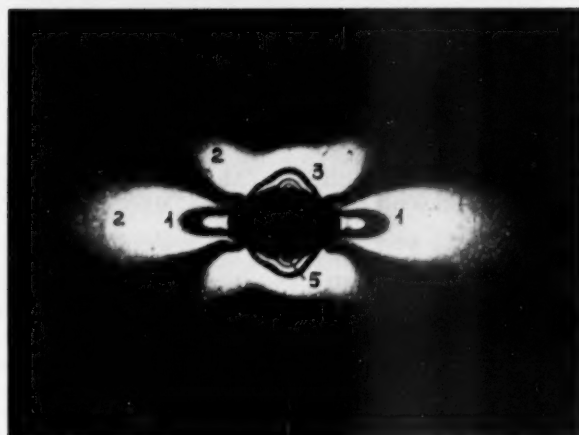
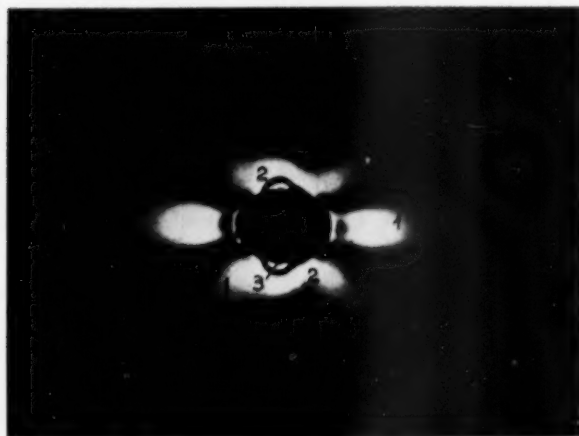


FIG. 4.—Deformation by simple tension ϵ_p and by simple compression ϵ_c as a function of the order of the fringe (not taking into account variations in the thickness of the test-specimens). The abscissa indicates the order of fringe/thickness.



FIGS. 5, 6, and 7.—Disks of 10 mm. diameter not bonded to the rubber and located at the middle point of the test-strips. Fringes of test-strips stretched 10, 20, and 40 per cent, respectively.



FIGS. 8, 9, and 10.—Disks of 2 mm. diameter not bonded to the rubber and located at the middle point of the test-strips. Fringes of test-strips stretched 10, 20, and 40 per cent, respectively.

Figure 4 the relations between strain by simple tension ϵ_t or compression ϵ_c and the orders of the fringes visible in polarized light for a prismatic test-specimen are indicated.

The trend of these relations is not linear; however, account must be taken of the fact that the thickness of a test-specimen changes, whether it happens to be stretched or compressed. Nevertheless, the curves make it possible to determine the local strains at those points on the test-specimen where the material can be regarded as under stress, whether this is simple tension or compression, and in particular on the boundary where no external load is applied.

DIMENSIONS OF THE TEST-SPECIMENS

The case of granules.—Strips of $200 \times 100 \times 2.2$ mm. were prepared; in them were inserted metal disks of different diameters (2 and 10 mm.) and 2.2 mm. thick, and having their faces in the same plane as the 200×100 mm. faces of the rubber, and with their rims simply in contact with the rubber or rigidly bonded to it. The locations selected for the disks are those indicated in Figures 1a and 1b.

The case of incision.—Strips of rubber of dimensions $200 \times 30 \times 2.2$ mm. were prepared, and in them were made incisions 5 mm. and 10 mm. long in the center part of their 200×30 mm. faces (see Figure 2) or laterally, starting from the side edge of the test-specimen (see Figure 3).

RESULTS AND EXPERIMENTAL OBSERVATIONS WITH THE DISK TEST-SPECIMENS

DISKS NOT BONDED TO THE RUBBER

Each test-strip was stretched 10, 20, and 40 per cent, elongations which were all measured between two marks at a distance of 50 mm. from the center of the disk and on both sides.

Figures 5, 6, and 7 show the fringes which form around the disks of 10 mm. diameter for the three elongations mentioned. Figures 8, 9, and 10 show the fringes which form around the disks of 2 mm. diameter, enlarged so as to be directly comparable with the preceding results.

The positions of the disks are such that the disturbance created by their presence does not extend to the outer edge of the test-strip. At its points of contact with the metal disks, the rubber is strained by complex forces which are difficult to define, since the disks introduce a discontinuity, with corresponding variations in the applied system of loads which are practically indeterminable. One must, therefore, be satisfied with the orders of the fringes, even if, under these conditions, they give only a qualitative indication of the local strain. Nevertheless, it could be demonstrated that, based on the curves in Figure 4 and the thickness of the test-strip, at elongations of 10, 20, and 40 per cent, the fringes would be of the orders of 1, 2, and 3.8, respectively. Test-strips which do not contain disks would be expected to be covered uniformly by fringes of these orders.

However, the maximum value of the fringe order in the neighborhood of the disks is actually 3, 5, and 11, respectively, for the three elongations, both for disks of 10 mm. diameter and for those of 2 mm. diameter. These values give an indication of the local stress concentration.

The distribution of the fringes around disks of 10 mm. diameter is practically

identical to that around disks of 2 mm. diameter, provided, naturally, that the elongations are the same in the two cases. The maximum orders reached locally in the most highly deformed zone are practically equal in the two cases.

It would have been interesting to examine test-strips containing still smaller metal disks, but experimental difficulties would have been encountered and the observations would have been laborious because, even for the cases described, the use of a microscope would have been necessary for observing the phenomena.

According to what was observed, the local state of deformation around a disk not bonded to the rubber does not depend on the dimensions of the disk itself. Moreover, even if extrapolation of this observation to very small diameters, i.e., to dimensions of the same order as those of the granules which may be found under practical conditions, might appear to be a bold step, it is at least easy to see that the presence of granules in vulcanized rubber is definitely a potential danger.

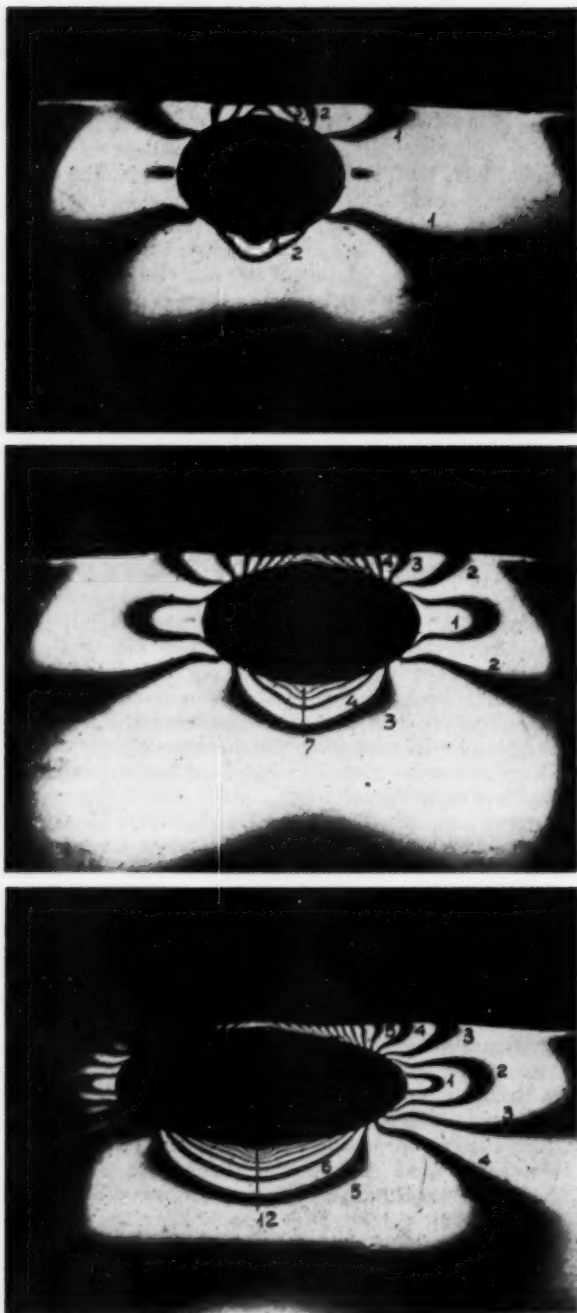
Figures 11, 12, and 13 show the fringes which are formed when the disk is 10 mm. in diameter and is at a distance of 1 mm. from the outer edge of the test-strip (see Figure 1b). A limited zone of this outer border is covered by a fringe of the quarter, tenth, and eighteenth orders, according to whether the test-strip is stretched 10, 20, or 40 per cent. These orders are considerably higher than those observed in the preceding cases.

Assuming that at the boundary of this zone, the material is, from a practical viewpoint, under simple tension, the local deformations can be readily determined. In the first two cases these are about 40 and 135 per cent; in the third case they are greater than 200 per cent, and they are certainly largely beyond the characteristic curve of the same material (see Figure 4). Presumably for elongations of the test-strips of 100 and 150 per cent and for greatly reduced distances of the granule from the edge, local deformations are reached which are dangerous even for static conditions. It has been found that the results of the observations are not altered even when the disks are of only 2 mm. diameter, provided that the distance between the edge of the test-strip and the periphery of the disk is reduced proportionally.

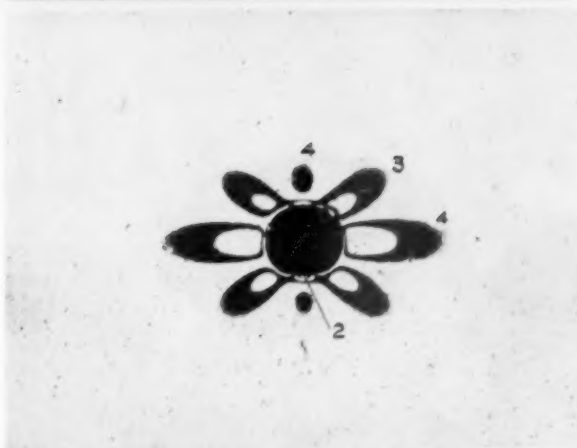
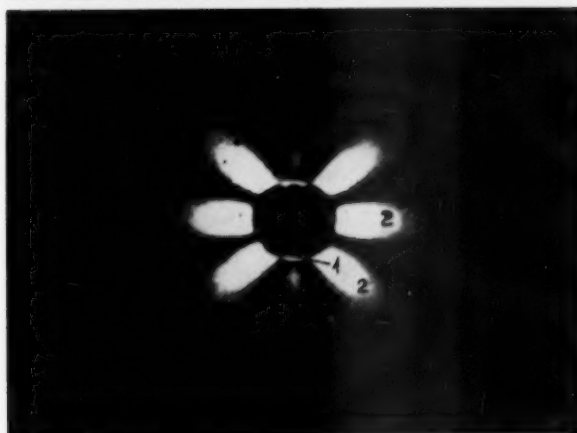
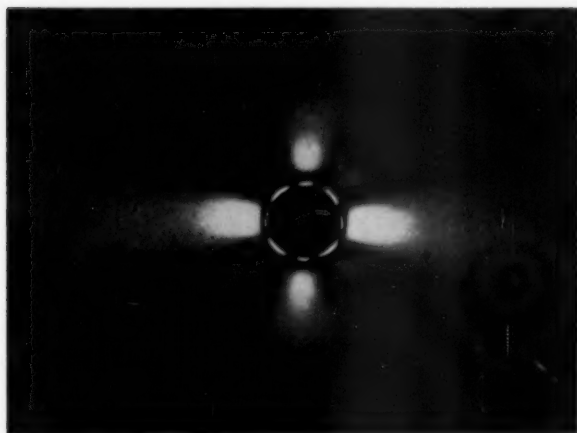
In tensile fatigue tests carried out on a De Mattia machine, with rectilinear test-specimens, and with the deformation cycle passing through zero deformation, phenomena were observed which may confirm what has been said above. After a certain number of cycles, there were observed on the surface of the rubber, by means of a microscope, lesions which, in some cases, revealed in the interior a definite crystal or a granule, or at least indications of their presence. It was proved that these lesions, in which there is an increased stress concentration, tend to enlarge rapidly until complete tearing of the test-specimen takes place as a result of fatigue.

The tests, which were rapid ones, i.e., from one to ten hours, were made at room temperature under such conditions as to reduce to a minimum any influence of heat, light, and ozone present in normal proportions in the air. Any lesions caused by ozone, though visible microscopically and though spread over the entire surface of the test-specimen, were practically negligible.

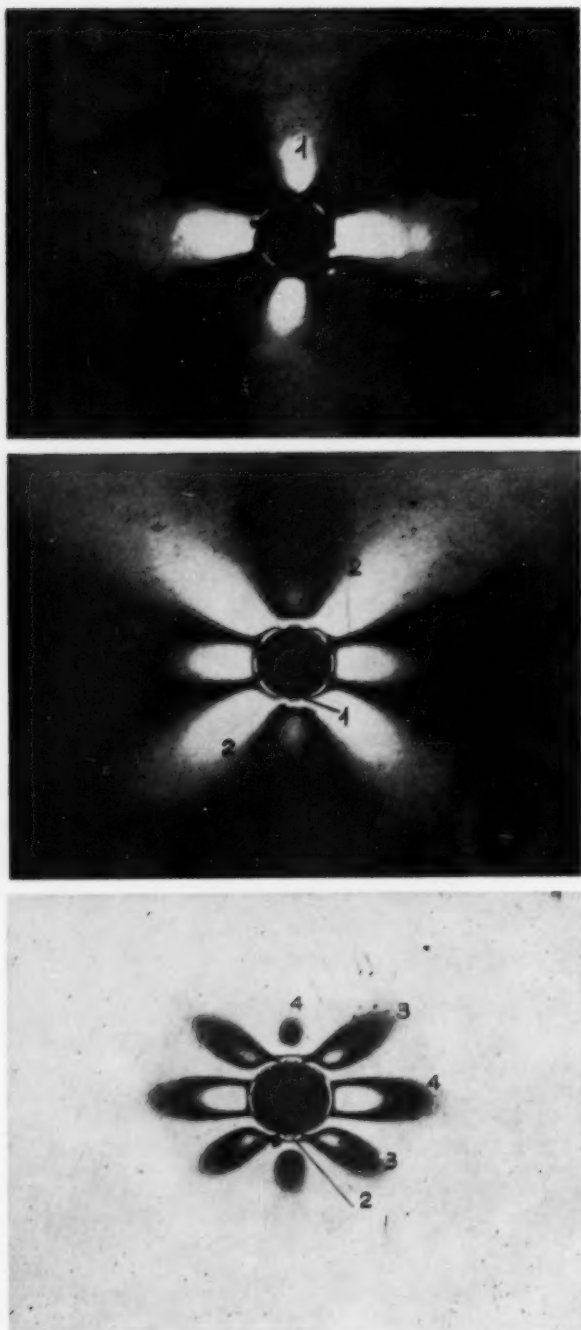
On the other hand, some observations, which were made only with considerable difficulty, of the interior of test-specimens subjected to dynamic stresses for a prolonged time, brought to light, in the neighborhood of crystals or granules, lesions whose dimensions were considerably smaller than those observed on the surface. It can, therefore, be concluded with some justification that the presence of granules of extraneous material located almost at the sur-



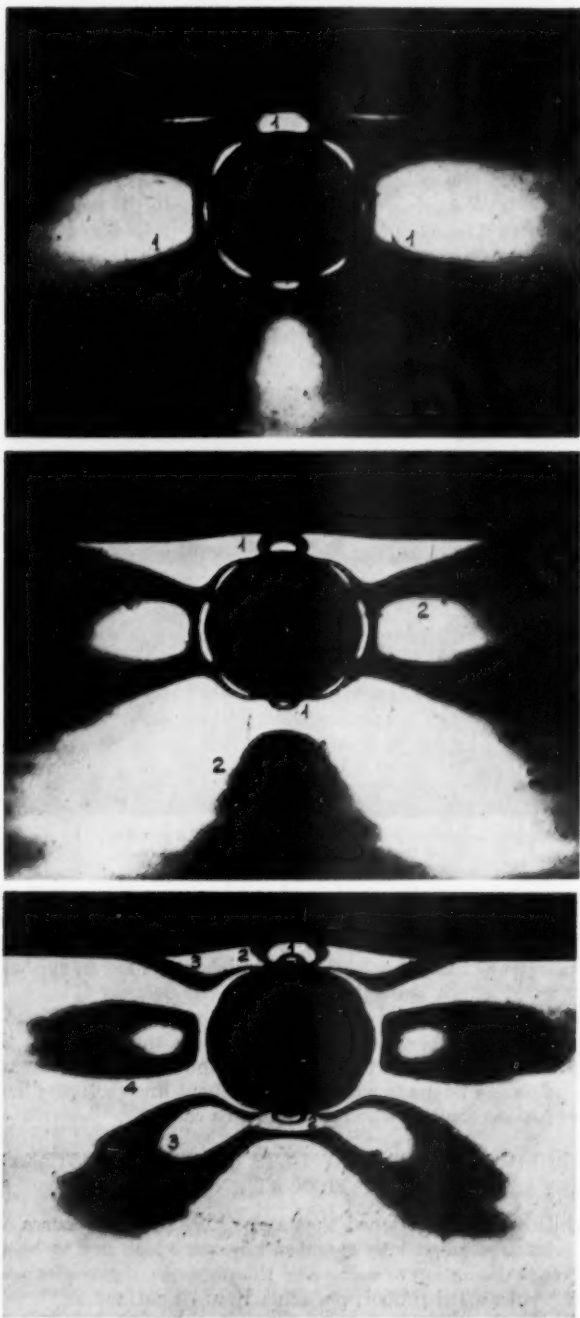
FIGS. 11, 12, and 13.—Disks of 10 mm. diameter not bonded to the rubber and located near the lateral edges of the test-strips. Fringes of test-strips stretched 10, 20, and 40 per cent, respectively.



FIGS. 14, 15, and 16.—Disks of 10 mm. diameter bonded to the rubber and located at the center point of the test-strip. Fringes of test-strips stretched 10, 20, and 40 per cent, respectively.



FIGS. 17, 18, and 19.—Disks of 2 mm. diameter bonded to the rubber and located at the center point of the test-strip. Fringes of test-strip stretched 10, 20, and 40 per cent, respectively.



FIGS. 20, 21, and 22.—Disks of 10 mm. diameter bonded to the rubber and located near the lateral edges of the test-strips. Fringes of test-strips stretched 10, 20, and 40 per cent.

face of rubber articles which are stressed dynamically cause local deformations which are of more serious consequence than those caused by granules located further in the interior.

DISKS BONDED TO THE RUBBER

Figures 14 to 22 show results when the disks are bonded to the rubber around their periphery. The maximum local deformations in the neighborhood of the disks are smaller than in the preceding case, as can be deduced from the orders of the fringes shown in the figures. The test-strips are, in addition, somewhat stiffer in the longitudinal direction. The maximum local order of a fringe remains practically unaltered with decrease of the diameter of the disks. This would seem to be true for diameters less than 2 mm., as was proved by actual tests under these conditions.

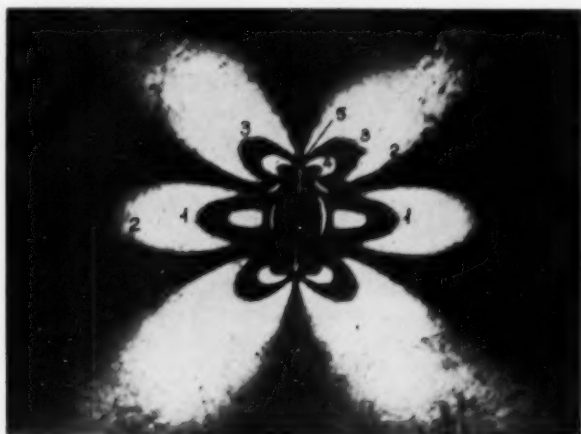


FIG. 23.—Incision of 5 mm. at the center point of a test-strip. Fringes of the test-strip stretched 20 per cent.

The presence of disks almost at the boundary (see Figures 20, 21, and 22) does not bring about any great local concentration of stress, as in the preceding case. Nevertheless, it seems probable that disks bounded to rubber represent a different case from that of a foreign material imbedded in rubber, which is generally regarded as not bonded to it.

The differences which were observed between disks bonded and disks not bonded to vulcanized rubber indicate, in addition, the likelihood that coarse fillers adhere by their surfaces to vulcanized rubber in a most tenacious way. No such assertion can be made with certainty about fine (active) fillers, and the present observations are not wholly true of this case.

OBSERVATIONS AND RESULTS CONCERNING STRESS CONCENTRATION AT AN INCISION

It has already been mentioned that among the primary causes of cracking of a test-specimen subjected to repeated stresses which are to be taken into consideration are the action of ozone and the presence of granules or impurities present in the vulcanized rubber, particularly in its surface.

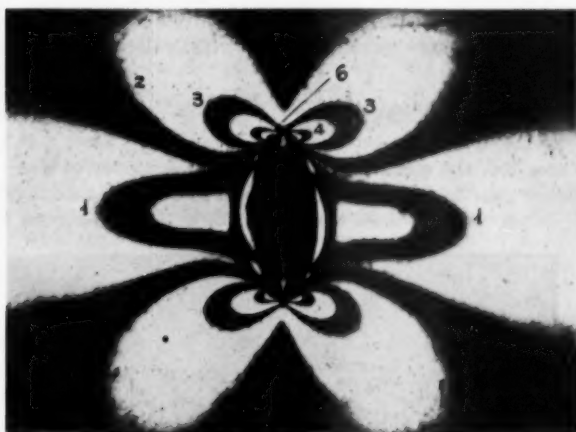


FIG. 24.—Incision of 10 mm. at the center point of a test-strip. Fringes of the test-strip stretched 20 per cent.

It next seemed desirable to examine the order of magnitude of the concentration of stress which is generated around incisions, already started, as a function of the dimensions of the incisions. The results obtained are of such a character as not to warrant any generalities, for they depend greatly on the dimensions of the test-specimen.

With the photoelastic method, the results would be expected to be quantitatively exact, since the deepest part of the incisions are subjected only to simple tension. Nevertheless, the deformations increase in the interior of an incision, with a very rapid gradient, and it is difficult to estimate the orders of the

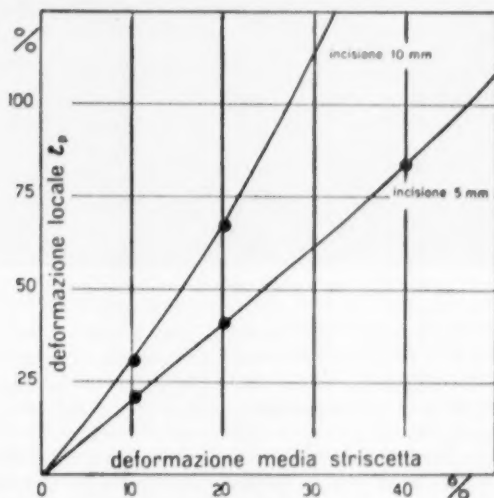


FIG. 25.—Local strain by tension for incisions of 5 and 10 mm. located at the center points of test-strips as a function of the mean elongation of the strips.

fringes, even with the aid of a microscope. In view of the way in which an incision is made, the edges represent a geometrically ill-defined zone of deformations.

INCISIONS AT THE CENTER OF A TEST-STRIP
(FIGURE 2)

In this case too, the mean deformations of each test-strip were 10, 20, and 40 per cent elongation, measured between marks 50 mm. distant from the axis of incision. Figures 23 and 24 show the zones of the incisions in two test-

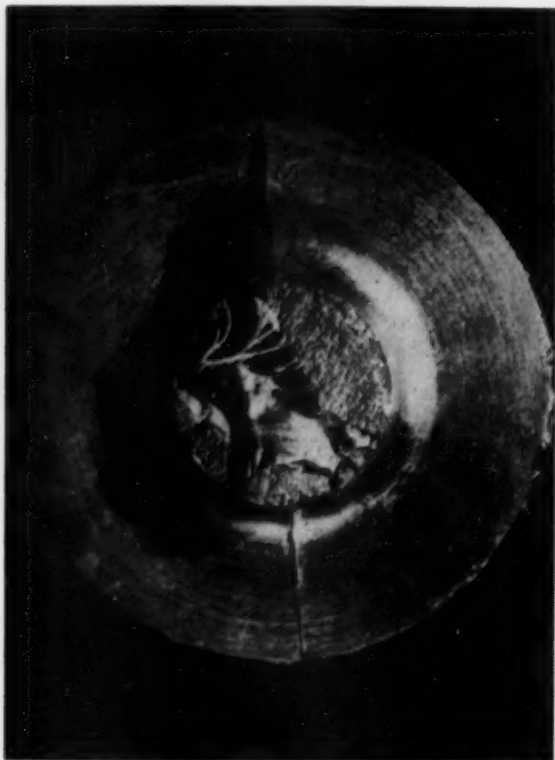


FIG. 26.—Rupture of a test-specimen by fatigue.

strips stretched 20 per cent. The incisions were 5 and 10 mm. long, respectively. The curves in Figure 25 show the local strain for simple tension ϵ_s of the material at the point of greatest stress (indicated by arrows in Figures 23 and 24) as a function of the mean deformation of the test-strip. The trends must still be regarded as indicative in view of what has already been said above.

The maximum local strains reached are much higher than the elongation to which the test-strip itself was subjected. In any case the maximum local strains are such that one can exclude the possibility that the growth of an incision of these dimensions resulting from fatigue stressing depends on the fact

that, at any cycle, the elongation at break of the material is reached. To explain the progress of these incisions with time, which happens even when test-specimens are fatigue-stressed in an inert gas, account must be taken of another phenomenon, which probably involves progressive local breaking of a certain number of bonds in the material at every stress cycle. When the growth of an incision reaches a stage where the local conditions are those of tensile rupture, then tear is instantaneous.

Figure 26 shows the surface of rupture of a test-specimen⁵ fatigued by tension in an atmosphere of nitrogen. A zone is visible where the tears have grown slowly with time (the opaque zone), as well as another zone (the clear zone) where rupture was instantaneous. This behavior resembles the behavior of a similar metal test-specimen.

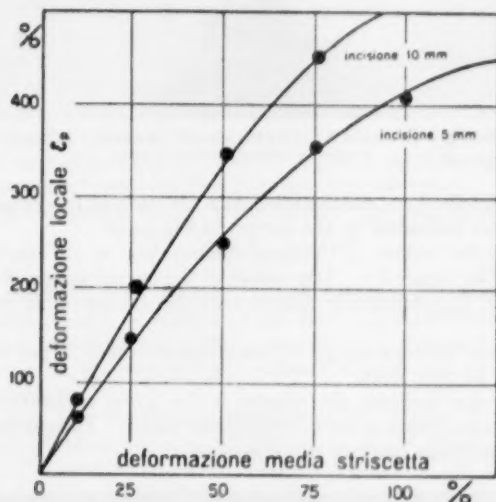


Fig. 27.—Local strain by tension for incisions of 5 and 10 mm., respectively, located at the center points of test-strips as a function of the mean elongation of the strips.

INCISIONS PERPENDICULAR TO THE OUTER EDGE OF A TEST-STRIP (FIGURE 3)

Finally let us consider test-strips of the usual dimensions subjected to tension and having incisions 5 and 10 mm. deep, respectively, perpendicular to their outer edges.

The maximum local strain cannot, in this case, be determined from the order of the fringes, because there is such an excessive number of these localized in a very restricted zone. However, it is possible to measure, with a certain degree of approximation, the local strain in the direction of stretching in the zone deepest in the incision by determining, at that point, the contraction of thickness of the test-strip by means of a microscope with ocular reticule.

This measurement can be regarded as correct, since the material in the interior of the incision where no external load is applied, is subjected to simple tension and since vulcanized rubber changes only to an insignificant degree in volume when it is deformed.

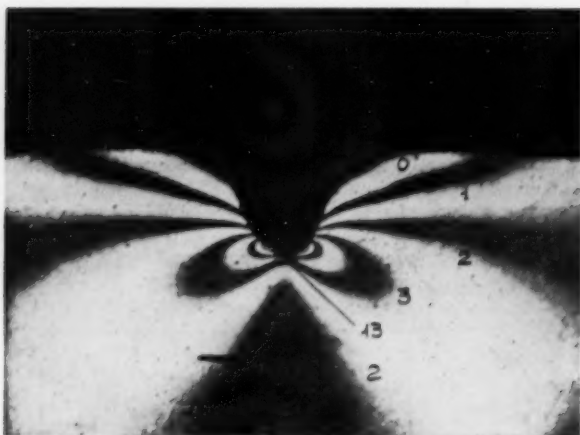


FIG. 28.—Incision of 5 mm. at the edge of a test-strip. Fringes of a test-strip stretched 20 per cent.

The values of the local deformation as a function of the mean elongation in the test-strip are indicated by the curves in Figure 27.

In this case the values of the local deformation ϵ_s are much greater than those indicated in Figure 25. The course of the curves makes obvious the non-linearity of the dynamometric diagram of the rubber mixture used for the models.

Figures 28 and 29 show fringes of test-strips stretched 20 per cent and having incisions 5 and 10 mm. deep.

The deeper the incision, the greater is the stress concentration and, consequently, the more rapid is the growth of the lesion. Fatigue tests carried out under these conditions confirm this observation.

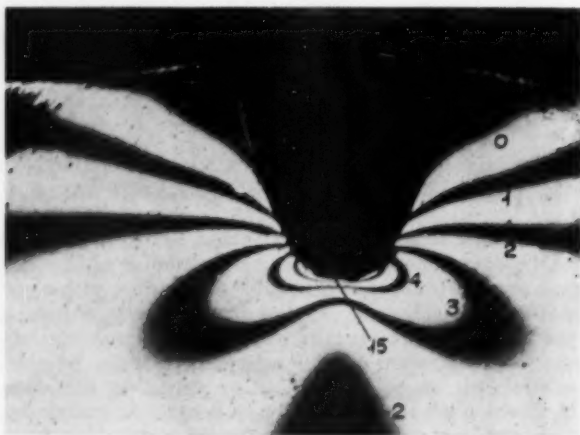


FIG. 29.—Incision of 10 mm. at the edge of a test-strip. Fringes of a test-strip stretched 20 per cent.

CONCLUSIONS

In this report, it is the intention to examine only a few of the aspects of the mechanism of fatigue of rubber objects subjected to dynamic stress. The phenomena which govern such fatigue are complex, and in some cases depend on factors which have a mutual influence, so that any analysis of them separately is difficult.

It is attempted to show the important part played by granules of foreign substances in vulcanized rubber and by any other impurities, even of the smallest dimensions, which may be instrumental (in conjunction with oxygen and atmospheric ozone) in forming lesions on the surfaces of rubber articles subjected to dynamic stressing, provided that there is no adhesion between these foreign substances and the surrounding rubber. On the other hand, whenever there is strong adhesion, the stress concentration is noticeably less and the possibility of local cracking is lessened.

In addition, the stress concentration which is set up where a lesion has already formed has been examined. Such lesions grow rapidly to the extent that complete rupture of the rubber article finally takes place.

Study of the laws and of the causes which start and govern the growth of incisions or of ruptures of any kind would require a more thorough examination of the intimate structures of different types of vulcanizates. It is intended to take up this problem eventually and to make it the subject of a future report.

SUMMARY

Poor dispersion of compounding ingredients, and the presence of granules and of impurities which in some way get into vulcanized rubber and thereby disturb the normal distribution of stresses in an article and thus cause local stress concentration, are regarded as accidental factors in the fatigue breakdown of vulcanized rubber.

This problem was studied by developing, by means of the photoelastic method, an adaptable schematic representation of the phenomena. Although only a qualitative evaluation of the local disturbance of the system of stresses caused by these factors is possible, in the particular case of granules, it has been found that the closer a granule is to the outside surface of the rubber article, the greater is the disturbance of the system of forces. Furthermore, the local stress concentration is greatest when there is no adhesion between the granules and the surrounding vulcanized rubber.

Finally the stress concentration caused by a small cut or incision made at various locations on a rubber test-strip under tension is considered. This case has been included because fatigue cracks first become manifest in this form.

REFERENCES

- ¹ Angioletti, *Kautschuk u. Gummi* **6**, WT-171 (1953); *RUBBER CHEM. & TECHNOL.* **27**, 839 (1954).
- ² Eecher, *Gomma* **4**, 1 (1940); *RUBBER CHEM. & TECHNOL.* **13**, 595 (1940); Le Bras and Salvetti, *Rev. gén. caoutchouc* **26**, 10 (1949); *RUBBER CHEM. & TECHNOL.* **22**, 690 (1949); Kuzminskii, Malzev, and Lezhner, *Doklady Akad. Nauk SSSR* **71**, 319 (1950); *RUBBER CHEM. & TECHNOL.* **24**, 250 (1951).
- ³ Naughton and Waring, *Trans. Inst. Rubber Ind.* **14**, 340 (1939); *RUBBER CHEM. & TECHNOL.* **12**, 845 (1939); Gul, Fedynkin, and Dogadkin, *Kolloid. Zhur.* **15**, 1 (1953); *RUBBER CHEM. & TECHNOL.* **27**, 363 (1954).
- ⁴ Shepard, Street, and Park, in "The Chemistry and Technology of Rubber", edited by Davis and Blake, New York, 1937, p. 380.
- ⁵ The sample for this test was prepared from a vulcanizate of natural rubber containing 40 per cent of MPC black.

MECHANICAL ACTIVATION OF THE OXIDATION OF VULCANIZATES BY STATIC AND DYNAMIC DEFORMATION *

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The deformation conditions to which rubber parts are subjected have a considerable effect, and in many cases the decisive effect, on their service life. One of us made a qualitative study which established the direct influence which the mechanical stresses created in a vulcanizate by dynamic deformation have on the rate of oxidative reactions¹. In the present work, a comparison was made between the effects of static and of dynamic deformation on the oxidation and breakdown of vulcanizates with differing structures².

Dogadkin and Tarasova³ established that vulcanizates with tetramethylthiuram disulfide form mainly monosulfide bonds. In vulcanizates containing diphenylguanidine, the presence of a large number of polysulfide bonds was noted. In a thermal vulcanizate, a spatial network with $-C-C-$ bonds was formed. All of the above vulcanizates were found to have approximately the same network densities, as determined from their equilibrium moduli⁴.

In order to remove the free ingredients remaining after vulcanization (free sulfur, accelerators, and phenyl-2-naphthylamine), all the vulcanizates before testing were extracted with acetone for 50 hours, in a stream of nitrogen, and were then dried in a vacuum. In experiments involving an antioxidant, the latter was introduced into the purified vulcanizate in a benzene solution. The thickness of the vulcanizate samples studied ranged from 0.2 to 0.25 mm. The work on dynamic deformation was carried out in a specially constructed apparatus, with a compensating mechanism for regulating the permanent set created under fatigue. It should be noted that in all the vulcanizates this accumulation of permanent set through fatigue was observed even in the first few cycles of the testing. The total amount of accumulated permanent set in a vulcanizate, from the time the testing began until the break, did not exceed 20-25 per cent of the original length of the sample. For the determination of the fatigue lives of vulcanizates, parallel tests were made on twenty-five samples⁵. A detailed investigation was made of the influence that the type of cross-links in the vulcanizates has on the fatigue lives of the latter.

In Table 1 a comparison is made of the lives of vulcanizates with different kinds of cross-links. The temperature of the test was 25° C, and the atmosphere nitrogen. The deformation conditions were a frequency of 250 cycles/min. and a strain amplitude of 75 per cent.

It is known that carbon bonds form a stronger network in vulcanizates than do sulfur (mono- and especially polysulfide) bonds. The data presented in Table 1 show that the lives of vulcanizates depend to a large extent upon the character of their cross-links.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by Malcolm Anderson from the *Doklady Akademii Nauk S.S.S.R.*, Vol. 93, No. 3, pages 519-522 (1953).

The life of the polysulfide vulcanizate was approximately fifteen times that of the thermal vulcanizate. It is characteristic that the change in structure in both types of vulcanizates with fatigue is revealed by an increase of the equilibrium modulus, in the range of 20–25 per cent.

Figure 1 compares the linear curves for the consumption of phenyl-2-naphthylamine in an unstrained vulcanizate with those for vulcanizates subjected to static and dynamic deformations.

TABLE 1

Type of cross-links in the vulcanizate	Equilibrium modulus (kg. per sq. cm.)		Fatigue life (cycles to break)	Fatigue life (minutes)
	Before fatigue	After fatigue		
Carbon ($-C-C-$)	4.6	5.1	4,150	16
Monosulfide	4.3	5.2	30,800	125
Polysulfide	5.0	6.2	62,820	252

Table 2 shows the effect of mechanical strains on the rate of consumption of phenyl-2-naphthylamine in the process of oxidation of vulcanizates with different structures. The temperature was 70° C, the atmosphere oxygen. The deformation conditions: static, 75 per cent deformation; dynamic, frequency of vibration 250 cycles/min., amplitude 75 per cent.

It is seen, from the data presented, that the mechanical stresses brought about by the deformation (static and dynamic) of vulcanizates have a considerable mechanical activating effect on the oxidation reaction. The gradient of mechanical stress remains at a higher level in vulcanizates under dynamic than

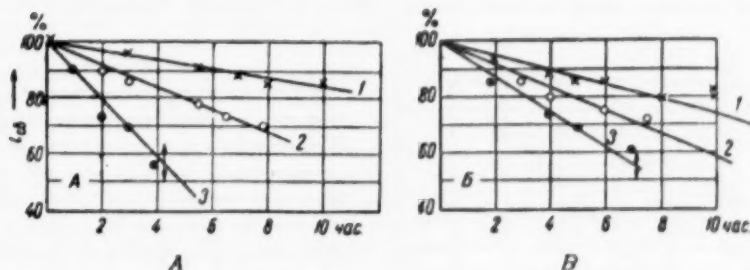


FIG. 1.—Kinetics of the consumption of phenyl-2-naphthylamine in the aging of a vulcanizate with tetramethylthiuram disulfide (A) and of a sulfur vulcanizate (B), at a temperature of 70° C. 1.—Aging in an unstrained condition. 2.—Aging under static strain (75 per cent elongation). 3.—Aging under dynamic deformation. The abscissas represent the time of aging in hours; the ordinates the free phenyl-2-naphthylamine content α expressed as percentage of the initial content. The arrows indicate the moment of rupture of the vulcanizate.

in those under static deformation⁶. The rate of oxidation of vulcanizates, in turn, depends directly on the amount of the stress. The mechanical activation effect, under given deformation conditions, depends to a large extent on the nature of the bonds which form the vulcanization network. When in a free unstrained condition, a vulcanizate with monosulfide (stable) bonds oxidizes at a slower rate than does a polysulfide vulcanizate. However, in strained vulcanizates the situation is different. Subjecting a monosulfide vulcanizate to static and dynamic deformations causes its rate of oxidation to increase to 1.3 and 4.5 times, respectively, that of the unstrained vulcanizate; whereas in the

TABLE 2

Type of vulcanizate	Rate of consumption of phenyl-2-naphthylamine ($w \times 10^{-2}$ millimole/liter/sec.)		
	Unstrained	Under static strain	Under dynamic deformation
Polysulfide	3.7	6.2	9.7
Monosulfide	2.5	4.9	11.3

polysulfide vulcanizate the rate increases only 1.6 and 2.6 times as much. The mobility of the polysulfide bonds in dynamic deformation facilitates a redistribution and an equalization of the stresses in the vulcanizate, which naturally depresses the mechanical activation effect and increases the fatigue life.

In another series of experiments, the effect of static deformation on the change in the mechanical properties of vulcanized stocks during oxidation was studied. Figure 2 shows the curves for the change of the equilibrium moduli in the course of the oxidation of unstrained and strained vulcanizates. Strained vulcanizates break much more quickly under oxidation than those oxidized in a free unstrained condition.

Since mechanical strains accelerate the breaking of vulcanizates to the same degree, whether they are heated in oxygen or in nitrogen, there is no basis for attributing this effect solely to the mechanical activation of the oxidation process. Apparently the deformation of a vulcanizate creates the necessary conditions for the formation on its surface of microcracks, which may deepen easily and thereby greatly reduce the strength of the material.

The ease with which polysulfide bonds decompose in the thermal oxidation of unstrained vulcanizates is a further cause of the formation of free radicals, and promotes aging in vulcanizates. Hence vulcanizates containing mainly

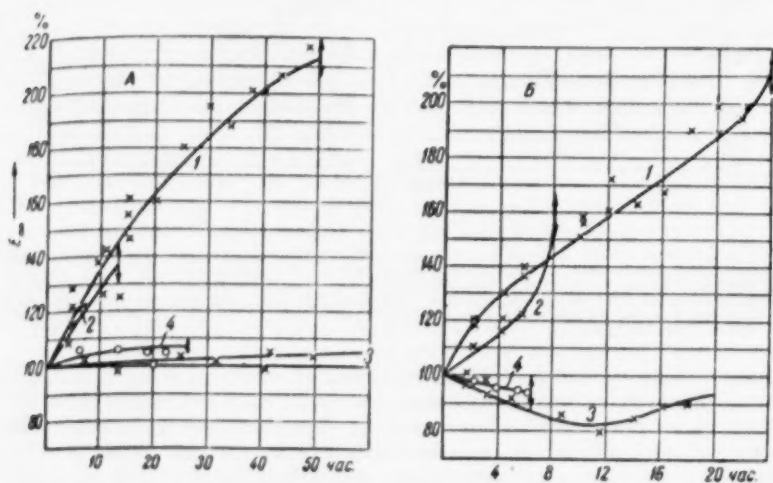


Fig. 2.—Kinetics of the change of the equilibrium modulus of vulcanizates heated in nitrogen (A) and in oxygen (B), at a temperature of 130°C. 1 and 2.—Vulcanizates containing mostly polysulfide bonds. 1.—Unstrained. 2.—Strained. 3 and 4.—Vulcanizates containing mostly monosulfide bonds. 3.—Unstrained. 4.—Strained. The abscissas represent the period of heating in hours; the ordinates the equilibrium modulus E_e expressed as percentage of the original modulus. The arrows indicate the moment of rupture of the vulcanizate.

polysulfide bonds, while they exhibit greater dynamic fatigue lives, are less stable toward oxidation in the unstrained condition.

As we have noted earlier¹, the presence of polysulfide bonds causes a considerable change in the structure of the vulcanizates even when they are heated in an atmosphere of nitrogen in a free unstrained condition. The structural changes which take place in vulcanizates heated in nitrogen occur entirely through the rupture and rearrangement of the sulfur bonds. The presence of mechanical strains in the vulcanizates has no effect, in this case, on the nature or the rate of such structural changes. When the vulcanizates are heated in oxygen, where both destruction and structure formation occur by means of oxygen combination, the application of a mechanical stress changes the ratio between the rates of the simultaneously occurring structure-forming and destructive reactions. As Figure 2B reveals, the modulus of a stressed vulcanizate increases at a slower rate than that of a free unstressed one, but its break occurs much earlier. This comes about through an increase of the rate of the destructive reactions.

The free radicals formed in the scission of the molecular chains of a vulcanizate can react in two directions. A reaction with oxygen and phenyl-2-naphthylamine amounts to an act of destruction (chain scission). A reaction with a double bond results in structure formation. In a stressed vulcanizate the chances are increased for a collision between a diffusing split-off end of a chain molecule (a free radical) and the low molecular-weight reaction products (from oxygen and phenyl-2-naphthylamine), the concentration of which is considerably lower than the double-bond concentration in the vulcanizate. The diffusion of split-off ends of polymer chains in a stressed vulcanizate may be likened to the agitation of reacting substances, or to a reaction taking place in a liquid stream. In vulcanizates containing polysulfide bonds, a destructive trend is noted during deformation. This trend is especially rapid when the vulcanizates are heated to 100° C and higher. After 10 hours at 130° C, the permanent set resulting from the destructive process reached 70 per cent. It was found that this process proceeds slowly even at 20° C; after one day the permanent set amounted to 15-20 per cent. This process naturally depends on the rupture and rearrangement of polysulfide bonds in the vulcanizates.

The experimental data presented here demonstrate that the mechanical activation of oxidation in vulcanizates is not only governed by the polymer structure, but also depends to a large degree on the nature of the cross-links which go to make up the vulcanization network.

REFERENCES

- ¹ Kuzminskii, Malsels and Leshnev, *Doklady Akad. Nauk SSSR* 71, 2, 319 (1950); Kuzminskii and Malsels, *Trudy Nauch.-Tekh. Konf. VNITO Resinshchikov* 1952, p. 106.
- ² The vulcanizates used in this research were based on the sodium-butadiene (polybutadiene) rubber SKB, and had the following recipes. I.—100 parts by weight of SKB, 2 parts of stearic acid and 1 part of phenyl-2-naphthylamine. II.—100 parts of SKB, 2 parts of stearic acid, 1 part of phenyl-2-naphthylamine, 5 parts of zinc oxide and 3 parts of tetraethylthiuran disulfide. III.—100 parts of SKB, 2 parts of stearic acid, 1 part of phenyl-2-naphthylamine, 5 parts of zinc oxide, 6 parts of sulfur and 1 part of diphenylguanidine. The vulcanization was done in a press at 143° C, for vulcanizates II and III, and at 220° for vulcanizate I (the thermal vulcanizate).
- ³ Dogadkin and Tarasova, *Doklady Akad. Nauk SSSR* 85, 5, 1009 (1952).
- ⁴ Bartenev, *Zhur. Tekh. Fiz.* 22, 7, 1154 (1952).
- ⁵ The deformation amplitude (75 per cent) was not over 15 per cent of the elongation of the vulcanizates at break.
- ⁶ A comparison of the effects of static and of dynamic deformation presupposes that the testing is done at the same temperatures and maximum deformations.
- ⁷ Kuzminskii and Lyubchanskaya, *Doklady Akad. Nauk SSSR* 90, 3, 409 (1953).

ABRASION AND FRICTION OF RUBBERLIKE MATERIALS *

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INTRODUCTION

Realization of the relation between abrasion and friction of rubberlike materials probably goes back to the early days of the development of synthetic rubbers of the oil-resistant type, such as Perbunan. Early investigators of compounds of these rubbers noticed extremely low abrasion losses (of the order of 1/20th to 1/40th of a natural-rubber tread compound) when tested on conventional laboratory abrasion machines. Road tests of experimental tires, however, did not confirm these low figures, and abrasion by high-speed grinding stones (25 meters per second or 56 miles per hour) was just as fast with these synthetic rubber tires as with the conventional rubber tread compound.

In the original Perbunan compound, considerable amounts of softener (30 parts of tricresyl phosphate) were used, and it was soon recognized that this caused some sort of lubrication of the rubber-abrader interface which resulted in a low coefficient of friction and prevented abrasion. Tires of this material were said to be extremely dangerous because of their tendency to slip, particularly on wet surfaces.

Abrasion at high speeds was probably rapid because of the large surface passing the rubber per second, which surface may have been too large to be wet by the amount of lubricant present, and the frictional heat may have caused the lubricant to evaporate. It is difficult to visualize which part of the rubber absorbs the abrasional forces and energy; in other words, what the thickness is of the layer that is directly affected by the rubbing process. These examples may serve to illustrate the problem with which we are concerned.

Many considerations have been given to measurements of abrasion resistance in the laboratory and, sometime in the history of this development, a conviction was established that it is impossible to rate materials according to their resistance to abrasion in general. The reason lies in the tremendous variation of conditions under which wear may occur even in one and the same application of one material.

We shall not go into the merits of various methods of rating any particular type of abrasion, but rather approach the problem from a different angle.

SCOPE OF THE PROBLEM

Abrasion of a soft material in contact with a hard one depends on forces interacting at the surface of the two materials. These forces, in turn, depend on the forces pressing the two surfaces together, on the speed of one surface relative to the other and, of course, on the nature of the surface of the materials.

* An English version, prepared by the authors, of the paper in *Kautschuk und Gummi*, Vol. 8, Special Issue on Tires, September, 1955, pages 45-48. This was presented at the International Conference on "The Tire" in Delft, Netherlands, May 12-13, 1955.

Considering only variations in the elastomeric member of the two rubbing partners, and maintaining the harder compound and the conditions of pressure and speed unchanged, the following is to be considered.

Forces acting on the rubber surface which tend to pull the surface layer away from the bulk of the material are transmitted to this material, which they deform, and thereby set up counteracting cohesive forces.

Abrasion is, therefore, dependent on two factors: (1) the development of a frictional force at the surface; (2) the counteraction of the rubbing force by the cohesive force in the rubber adjacent to the surface layer, if this force is strong enough to match the frictional force.

Abrasion resistance is high when factor (1) is low and factor (2) is high. But low (1) is undesirable from the viewpoint of the tire manufacturer or the car driver, since it means low coefficient of friction, with resulting lack of grip on the road and, consequently, increased likelihood of slipping. Therefore, improved abrasion must come from an increase of item (2); i.e., an increase of the cohesive forces inside the rubber.

The question may be raised whether or not it is possible to improve abrasion by an increase of the cohesive forces (2) without reducing at the same time the frictional forces and, if so, to what degree. If it is possible, we may be fairly certain that this cannot continue indefinitely; sooner or later interference with the forces active on the surface must follow, with a resulting decrease of the coefficient of friction. When all intermolecular forces are saturated by mutual interaction of the polymer molecules no forces or only small outwardly directed forces will appear (low adhesion and friction).

This problem is of great interest to manufacturers of reinforcing pigments in connection with materials like polyurethans or polyisocyanate polyester rubbers. These are extremely tough, with abrasion resistance higher than that of conventional treads of rubber and reinforcing carbon black. The problem we are going to consider is how, under certain experimental conditions, abrasion and coefficients of friction influence each other.

RELATION BETWEEN ABRASION AND COEFFICIENT OF FRICTION

It is not possible to indicate with certainty what molecular factors affect the coefficient of friction of polymeric materials on a hard surface, but cohesion energy density must be one of the factors involved, and another is regularity of structure, which may be equally important. Loose mobile chain ends probably cause high friction and the same is true of polar groups interacting with similar groups on the wearing surface.

The relation between friction force and load of elastomers is not a straight proportionality; it has been studied by Thirion¹ who developed the formula:

$\frac{1}{\mu} = a + bL$, which was checked by Denny² over a 10,000-fold load range.

Schallamach³, Lincoln⁴, and Bowden⁵ showed proportionality between friction force and true area of contact, both varied as L^{-1} for an elastic hemisphere.

Ratner and Sokolskaya⁶ published the formula: $\mu = \mu_{\infty} + \frac{A}{L}$, in which μ_{∞} is the friction for infinitely high load. μ_{∞} depends only on the surface of the material on which the rubber runs, L is the load, and A is a constant. They found that fillers generally decrease the constant A as long as they are completely surrounded by rubber.

Apparently all these conditions are different from ours, where abrasion occurs. Though our range of loads is very small, it shows a deviation from Thirion's law, and increasing proportions of carbon black increase the coefficient of friction, contrary to the observations of Ratner and Sokolskaya.

Bowers, Clinton, and Zisman⁷ found a relationship between the shearing strength of the bulk material for a number of plastics, particularly derivatives of polyethylene. They found the frictional force: $F = s \cdot a$, where s = shear strength of the plastic, a = true area of contact; furthermore, $\mu = s/p$ (p = yield pressure). The correlation, however, is only a rough one (within a factor of 2).

EXPERIMENTAL CONDITIONS

The experimental conditions were as follows. Motor-driven disk-shaped test-pieces run on a grinding wheel, which is braked by electromagnetic clutches. The braking torque is measured, and the speed differential is determined continuously. The pressure of the sample on the grinding wheel is adjustable.

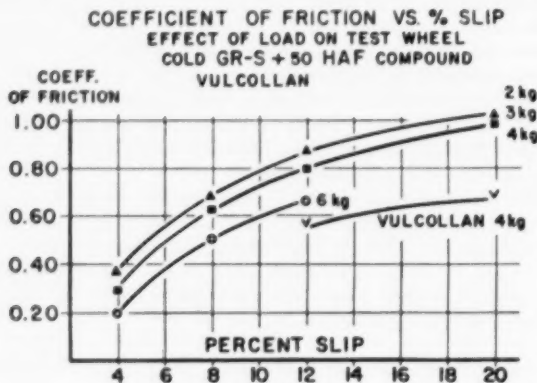


FIG. 1.

With the aid of this machine, we are able to determine abrasion losses under various conditions of pressure and differential speed, which conditions cause differences in the coefficient of friction. These differences take variable courses for various compounds. One way of eliminating their effect in a first approximation is to express abrasion in terms of efficiency of abrasion; in other words, the abrasion loss per unit energy spent on the surface. This energy and also the coefficient of friction can be easily determined. This eliminates part of the lubrication effect which may occur on the stone. When the test wheel is slipping lightly over the lubricated stone, only a small torque is registered and, as a consequence, little energy is spent on abrasion. This does not eliminate the effect completely, as is shown by the Grasselli abrasion machine, which also works on the same basis but still shows low values for Perbunan rubbers.

DEPENDENCE OF THE COEFFICIENT OF FRICTION ON THE LOAD AND SLIPPAGE

First of all, it is of interest to see how the coefficient of friction changes with the load and slip of a tire-tread compound. This is shown in Figure 1. Figure

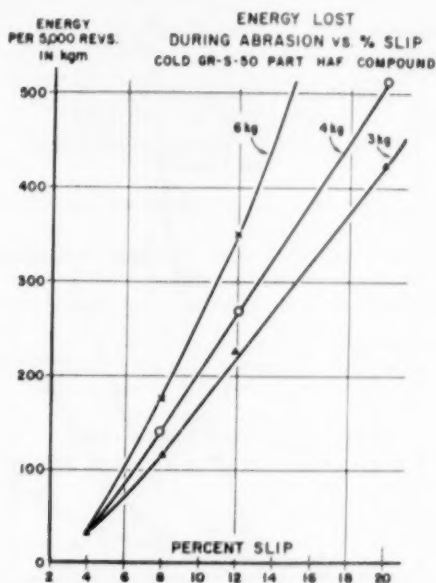


Fig. 2.

1 shows that the percentage slip offers a convenient means of varying the friction.

The energy as a function of percentage slip shows an almost linear increase, as indicated in Figure 2.

Figure 3 shows the effect of carbon black loading on friction.

It has been shown in a number of short runs that no significant changes in coefficient of friction occur when the number of revolutions of the sample is increased from 450 rpm to 610 rpm. All measurements have been carried out at 610 rpm.

It is interesting to follow the change of abrasion efficiency (mg. loss per kg., energy lost on friction) as a function of the coefficient of friction for cold GR-S compounds containing various proportions of carbon black. This is shown in Figure 4.

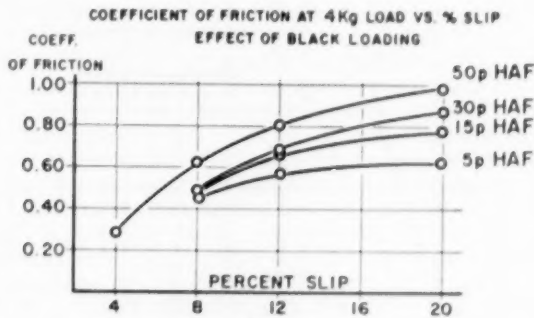


Fig. 3.

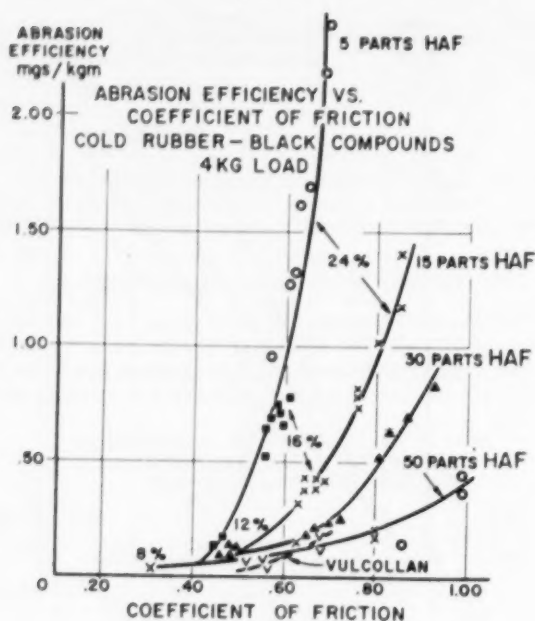


FIG. 4.

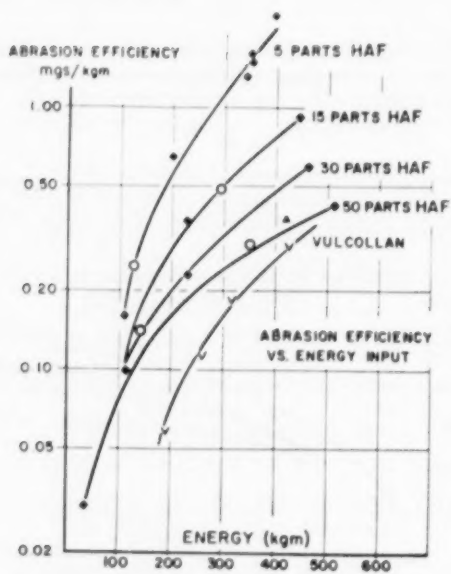


FIG. 5.

For GR-S containing only 5 parts of HAF black (fine-particle reinforcing oil furnace black), at a coefficient of friction nearing 0.60, the abrasion efficiency goes up steeply. When the loading with reinforcing black is increased to about 15, a much higher coefficient of friction may be attained without immediately rubbing off the material completely. With 30 and 50 parts load, the abrasion efficiency is much lower, and a higher friction (of over 1.00) coefficient may be reached.

It is remarkable to see how all the curves come together at the low friction values.

In Figure 4 a number of results with Vulcollan have also been entered. These apparently show a possible lower efficiency of abrasion than the GR-S compound containing 50 parts of HAF black at low coefficient of friction, but the differences are not convincing.

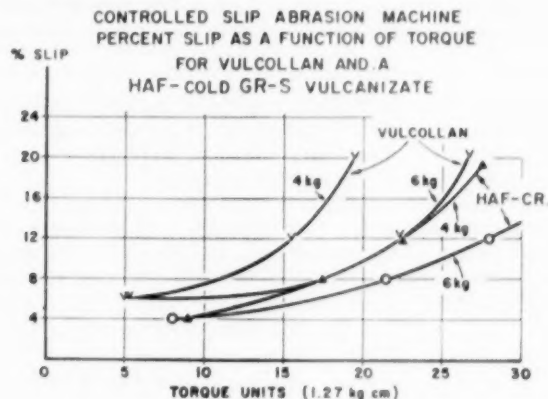


FIG. 6.

A better differentiation is shown in Figure 5, where the abrasion efficiency is plotted against energy spent on abrasion. Since the test takes the same time in all cases, this energy also indicates the power or intensity of abrasion. It is obvious that, for the same power absorption, the abrasion of the Vulcollan sample is less than that of any of the other compounds. These other compounds are the GR-S vulcanizates containing 5, 15, 30, and 50 parts of HAF black, and they show the same increase of abrasion resistance with higher black loading when compared at one power level.

The difference between the rubber-carbon black compounds and Vulcollan is hidden in the way the abrasion energy is generated. For the Vulcollan rubber, a much higher percentage slip is necessary to obtain the same energy generation than for the rubber-carbon black compound. This is shown in Figure 6, where the percentage slip is plotted against the torque generated at two loads, 4 and 6 kilograms. To obtain the same torque, a much higher percentage slip is necessary for Vulcollan than for the conventional cold GR-S compound containing 50 parts of carbon black. In other words, with the same slip, less torque is obtained with Vulcollan than with the rubber-carbon black compound. The disadvantages of this for Vulcollan are obvious.

We have tried to determine the effect of carbon black on the coefficient of friction of elastomer compounds of the Vulcollan type. The results of these

TABLE I

	Mix	Shore hardness	Coefficient of friction		Abrasion loss	
			18% Slip	24% Slip	18% Slip	24% Slip
I	Pure-gum Vulcollan	75	0.62	0.63	0.12	0.20
II	Polyester isocyanate 5% black	65	0.79	0.83	0.52	0.67
III	Product with 25% black	98	0.73-0.79	0.81	0.02*	0.01*
	GR-S tread stock	65	0.87	0.98	0.25	0.4

* Samples became sticky.

measurements are listed in Table I. In evaluating the data, it should be considered that the three compounds were made by entirely different manufacturers, so there may be large differences in the base polymers. This obscures the effect of the different percentages of carbon black in these compounds. In compound II, for instance, the coefficient of friction has increased over that of the pure-gum vulcanizate, but the abrasion loss is also considerably higher.

SUMMARY

The relationship between abrasion resistance and the coefficient of friction was observed in the early days of development of the modern synthetic rubbers. It has gained new interest in connection with the appearance on the market of polyester-isocyanate rubbers of the Vulcollan type.

The abrasion of a rubber object in contact with a solid depends on the forces interacting at the surface of the two materials. These forces are again dependent on the forces pressing the two surfaces together, on the relative surface speed of the one object with respect to the other, and on the nature of the surfaces of the materials. Forces acting on the rubber surface and tending to pull the surface layer away from the bulk of the material deform the bulk rubber and excite counteracting cohesive forces.

Abrasion of the rubber depends on the following two factors:

- 1) Development of frictional forces at the surface.
- 2) Counteraction of the force caused by the rubbing by cohesive force in the polymer adjacent to the surface layer.

The question may be raised if it is possible to improve abrasion resistance by increasing the cohesive forces (1) without affecting the frictional forces and (2) if so, to what degree.

With the help of the modified Cabot-Lambourn abrader, a number of experiments have been carried out that give some answers to the correlation of abrasion and friction. Abrasion is measured in terms of abrasion efficiency, i.e., weight loss per unit of energy. Correlations are established between:

- (a) Coefficient of friction and normal load.
- (b) Coefficient of friction and percentage loss of weight.
- (c) Coefficient of friction and carbon black loading.
- (d) Abrasion efficiency, coefficient of friction, and carbon black loading.
- (e) Abrasion efficiency and energy spent on abrasion.
- (f) Percentage of slip and torque obtained.

REFERENCES

- ¹ Thirion, *Rev. gén. caoutchouc* **23**, 101 (1946).
- ² Denny, *Proc. Phys. Soc.* **B116**, 721 (1953).
- ³ Schallamach, *Proc. Phys. Soc.* **B116**, 386 (1953).
- ⁴ Lincoln, *Brit. J. Applied Physics* **3**, 260 (1952).
- ⁵ Bowden, Intern. Conf. on Abrasion and Wear, *Engineering* **172**, 724 (1951).
- ⁶ Ratner and Sokolskaya, *Doklady Akad. Nauk U.S.S.R.* **86**, 121 (1952).
- ⁷ Bowers, Clinton, and Zisman, *Modern Plastics* **31**, 34 (Feb. 1954).

PRINCIPAL CONSIDERATIONS ON TIRE WEAR *

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INFLUENCE OF TIRE ELASTICITY

The prerequisite for tire wear is relative motion between the tire and road in their common area of contact. Such relative motion occurs, for example, when a tire is flattened on entering the area of contact¹ and can also take place when the tire exerts a force on the ground, i.e., during propulsion, braking and, particularly, cornering. The mechanism of abrasion when the wheel is not rolling freely becomes complicated by the fact that, because of the elasticity of the tire, its circumferential velocity with respect to the vehicle can differ from the travelling velocity, and that, furthermore, the tire can have a velocity component normal to its plane without skidding. In other words, slip without noticeable abrasion is possible.

The only case discussed here will be when the wheel describes a curved path. The elasticity problem involved has been treated, among others, by Fromm², von Schlippe³, and Temple⁴; the essential facts are best visualized by means of the model experiment reproduced in Figure 1. In this experiment, a solid rubber wheel rolled around a Perspex disk, and the area of contact was illuminated by internal reflection. The deformation of the equator (marked in black) shows that two regions can be distinguished in the area of contact. In the front part, the equator is distorted into a curve parallel to the path, i.e., into a circle, and one can easily see that no relative motion between wheel and track occurs here, but that the wheel adheres to the track. The tangential stress necessary to deflect the wheel is maintained by friction until the stress becomes so high that the limiting friction is reached. At this point the second or rear part of the area of contact develops, in which the wheel slides back sideways. Abrasion should, therefore, be expected only in the rear part of the area of contact. It will decrease with increasing elasticity of the tire, but nothing will be gained thereby, since the tire has, after all, to take up the forces arising during driving. In the present case, this involves the side force holding the vehicle on the curve, and what matters is the dependence of abrasion on this side force.

Making simplifying assumptions, this problem can be treated theoretically for constant slip at a small slip angle. The result given below has been obtained with the aid of a method which is a modification of the method first applied by Turner⁵ to abrasion on the Akron machine. It is assumed that (1) the deflection of the tire is everywhere proportional to the tangential stress; (2) abrasion is proportional to the dissipated frictional work⁶, and (3) the area of contact is rectangular. The result depends then in detail on the pressure distribution, which, however, does not appear to influence the connection between wear and modulus. The following equation is valid for a pressure distribution elliptical

* An English version, in essentially the form prepared by the author, of a paper in *Kautschuk und Gummi*, Vol. 8, Special issue on tires, September 1955, pages 27-30.

in the circumferential direction and constant across the tire:

$$\text{abrasion} = \text{const} \frac{V}{G} (s^2 + \frac{1}{4}s^4 + \frac{1}{4}s^6 + \dots)$$

where V is the velocity; G , the shear modulus of the tire, and s the side force, expressed as a fraction of the maximum possible side force. According to this equation, wear at constant side force decreases with increasing stiffness of the tire, but it must not be forgotten that the modulus G refers to the whole cross-section of the tire and depends relatively little on the modulus of the tread. It

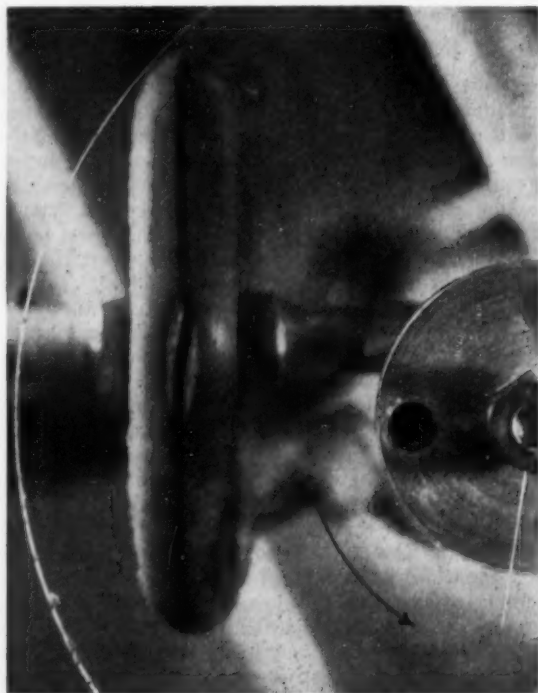


FIG. 1.—Model experiment to illustrate deformation and slip of a tire in a curve. Direction of motion counterclockwise.

will also be seen that wear increases rapidly with increasing velocity, since the side force balances in effect the centrifugal force and is, therefore, proportional to the square of the velocity.

Similar considerations can be applied to forces in the circumferential direction, e.g., braking, and lead to similar results.

THE MECHANISM OF WEAR

GENERAL

The constant in the equation above contains, among other factors, the wear resistance of the tread mix. Experience shows more and more that the relative

TABLE I

Cycle	45 MPC	45 UFF	60 MPC	60 UFF
B	12.9	13.9	14.8	18.1
C-F	14.5	17.4	17.7	18.3
G	28.7	28.9	23.8	24.2
H	12.2	12.7	14.5	13.5

wear resistance of two mixes has no generally valid magnitude, but depends on a number of variables, the most important of which are temperature⁷ and severity of the test⁸. We shall discuss here only the second factor. Particularly interesting in this connection is the following table from the paper by Buist, Newton, and Thornley, which gives road wear abrasions of four different tread mixes in 0.001 inch per 1000 miles. Each cycle comprises a complete rotation of the wheels, in which each tire ran in each wheel position; the tread mixes are specified by their carbon black content indicated at the head of the columns. In this experimental series, comparing mixes with two different fillers and two different filler contents, the higher loaded mixes gave, in general, higher abrasion figures. The figures for cycle *G*, in which conditions were obviously more severe than in the other cycles, are remarkable; under these exceptional conditions, the higher loaded and therefore stiffer mixes were less abraded than the softer mixes. Ranking of tread compounds can thus depend on details of the road test.

A hint as to the possible origin of such effects is given in Figure 2, taken from an earlier publication⁶. These two photographs show the surface of a typical tread mix abraded under laboratory conditions on rough and smooth concrete roads. The ridges seen in these pictures are called abrasion patterns, and are characteristic signs of the abrasion process. They are due to the combination of high elasticity and high coefficient of friction peculiar to rubber and have

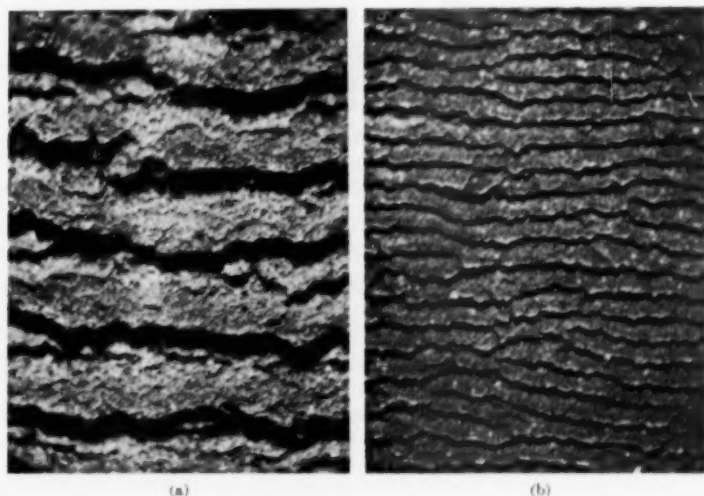


FIG. 2.—Abrasion patterns on a tread compound abraded on (a), a rough and (b), a smooth concrete road. Magnification 15 \times . (Schallamach⁶.)

already been described in detail⁹. It may be mentioned that the ridges are always at right angles to the direction of abrasion, that they increase abrasion, and that they are the coarser, the lower the modulus of the mix and the rougher the track. The last point is made clear by Figure 2. In this case, abrasion on the rough concrete was about four times higher than on the smooth concrete, a difference which must in part be ascribed to the ridges. Further examples of the influence of abrasion patterns on abrasion will be given later.

It may also be noted briefly that the orientation of abrasion patterns can give information on the mechanism of rolling tires¹⁰.

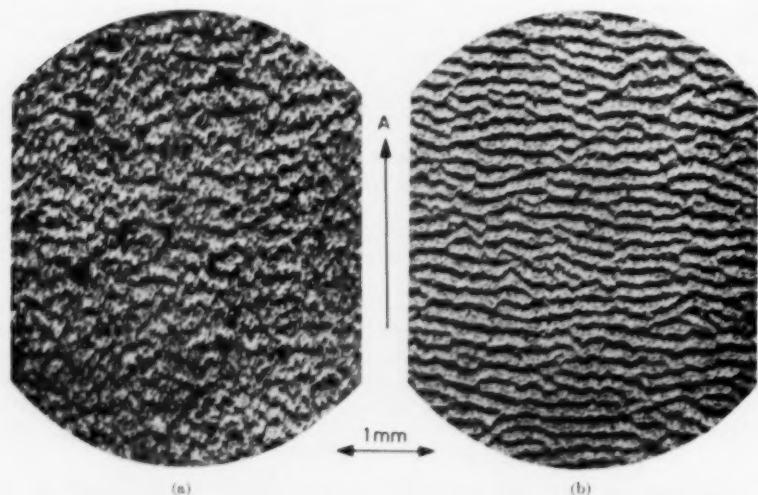


FIG. 3.—Surface of a tread compound abraded on (a), garnet paper, and (b) emery paper.

It must be kept in mind, however, that abrasion patterns are merely a concomitant effect of abrasion, and that abrasion without an abrasion pattern is possible. It is, therefore, suitable to consider tire wear as the outcome of two phenomena, intrinsic abrasion, and the propensity of the mix to form abrasion patterns.

INTRINSIC ABRASION

Intrinsic abrasion is the abrasion determined when the formation of abrasion patterns is prevented, and the influence of the elastic properties of the sample as already discussed is mostly eliminated, that is to say, when the sample is not subjected to a continuous rate of deformation during the experiment. This is easily achieved by abrading a flat sample on a plane track and changing the direction of abrasion periodically. It is also recommended that the sample be extracted before the experiment so that the results are not falsified by softeners, etc., which ooze out of the surface and contaminate the track.

Experiments on the nature of intrinsic abrasion were carried out some time ago¹¹. Rubber surfaces were scratched with a needle in order to study the effect of local stress concentrations such as are expected to occur where asperities

of the road or of the abrasive track impinge on the rubber surface. The needle traces, the details of which depended on the nature of the rubber, could be explained qualitatively and showed that abrasion, i.e., the mechanical detachment of small particles, could be a consequence of local stresses. Similar results⁶ are obtained when a blunt point instead of a needle is drawn over the rubber. The tangential stress produced by friction can, therefore, initiate tears on the rubber surface.

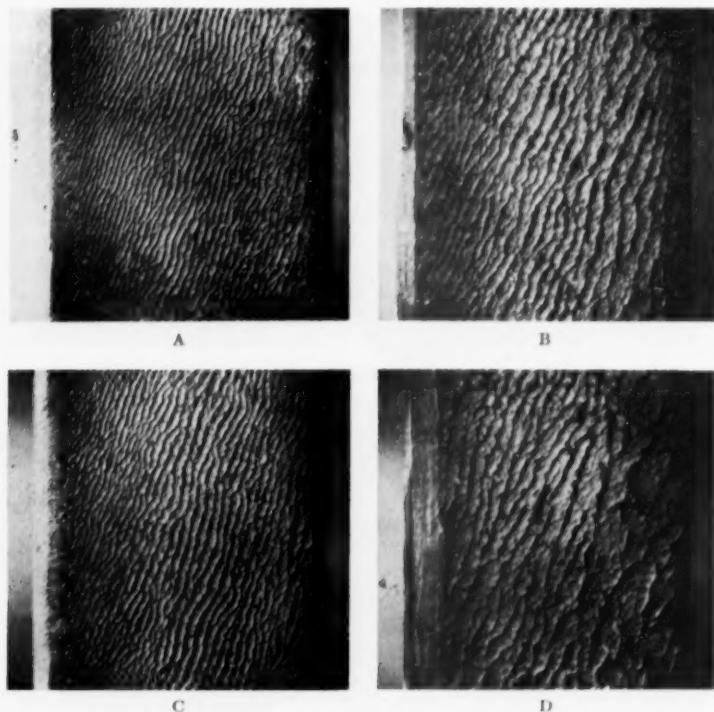


Fig. 4.—Akron samples of natural rubber with the following filler contents in parts per hundred: A, 45 HAF; B, 30 HAF; C, 45 SAF; D, 45 SAF. Magnification 3.5 \times .

A simple theory of intrinsic abrasion⁶ has been developed on such observations, starting from the assumption that abrasion resistance is ultimately governed by tear resistance. The theory predicts that abrasion is proportional to the normal load, is independent of the particle size on an abrasive with polyhedral particles, and proportional to the radius of curvature in the case of spherical particles. These predictions agree satisfactorily with the experimental results.

ABRASION PATTERNS

In every discussion of abrasion patterns, the following point has to be taken into consideration. Since abrasion patterns can form only if the modulus of the rubber is not too high, they can appear on conventional tread mixes only

after a surface layer of the sample or tire has suffered sufficient lowering of modulus through the combined effects of repeated local stresses of the kind described in the preceding section (Mullins effect¹²). This was surmised in the first description of abrasion patterns¹, has since been verified by other experiments¹³ and is to be illustrated here by a practical example. Figure 3 shows the same tread mix abraded on garnet and emery paper. The sharper garnet paper abrades the rubber so energetically that the softened surface layer is removed as soon as formed, and no abrasion pattern is produced; but on the blunter emery paper, abrasion is so slow that the condition for the formation of ridges is fulfilled.

Choice of a suitable abrasion method and suitable abrasive is, therefore, indicated when estimating the propensity of compounds for forming abrasion patterns. It has been found that the Akron-Croydon machine is well adapted for this purpose without materially affecting the results through the effects already discussed. Figure 4 gives examples of abrasion patterns produced on this apparatus. The difference between the surfaces of the mixes loaded with 30 and 45 parts per hundred of HAF black shows the influence of modulus on ridges mentioned earlier, and the difference between the two mixes loaded with 45 parts SAF black, compounded to different recipes, is explained by the higher coefficient of friction of mix D. It is interesting to compare in Table II the figures for abrasion on the Akron machine with the intrinsic abrasions of these compounds.

TABLE II

	A	B	C	D
Black loading pph	45 HAF	30 HAF	45 SAF	45 SAF
Intrinsic abrasion	100	104	99	85
Akron-abrasion	100	142	90	125

According to Table II, the relative abrasion resistance depends to a great extent on the method of measurement, and this can also alter the ranking. The figures for mixes A and B show a tendency already seen in Table I: the inferiority of the softer mix becomes evident only under the more severe conditions imposed by the Akron machine. Severity of the test must not be confused with sharpness of the abrasive; the grindstone of the Akron machine is actually blunter than the garnet paper on which the intrinsic abrasions were determined. What matters is that on the Akron machine abrasion patterns are formed and these accelerate the rate of abrasion.

PRACTICAL APPLICATIONS

The suggestion to take intrinsic abrasion and abrasion patterns as the essential factors in tire wear can now be reformulated as follows. The ratio of the wear figures of two given compounds will approach the ratio of the intrinsic abrasions if the road test is carried out under very mild conditions, under which the influence of abrasion patterns can be neglected. When the conditions are made more severe and the abrasion patterns contribute significantly to the wear, the absolute value of the abrasions naturally increase, but the ratio of the wear figures still depends on the propensities to form abrasion patterns and so, in practice, on the moduli. It is possible that even a reversal of ranking occurs, such as has been found by Buist, Newton, and Thornley.

The practical application of these concepts is still in its preliminary stages, and will be illustrated here only by a simple example.

It can so happen that the severity of the laboratory test is similar in intensity to that obtained in the road test. Figure 5 refers to an experimental three-way tire whose tread compounds were loaded, respectively, with 25, 35, and 45 parts per hundred of HAF black. The two photographs on the right-hand side show the surface of one of the running bands on the sectors loaded with 25 and 45 parts of HAF black; on the left-hand side, two extracted Akron samples of similar composition are shown for comparison. It is immediately seen that

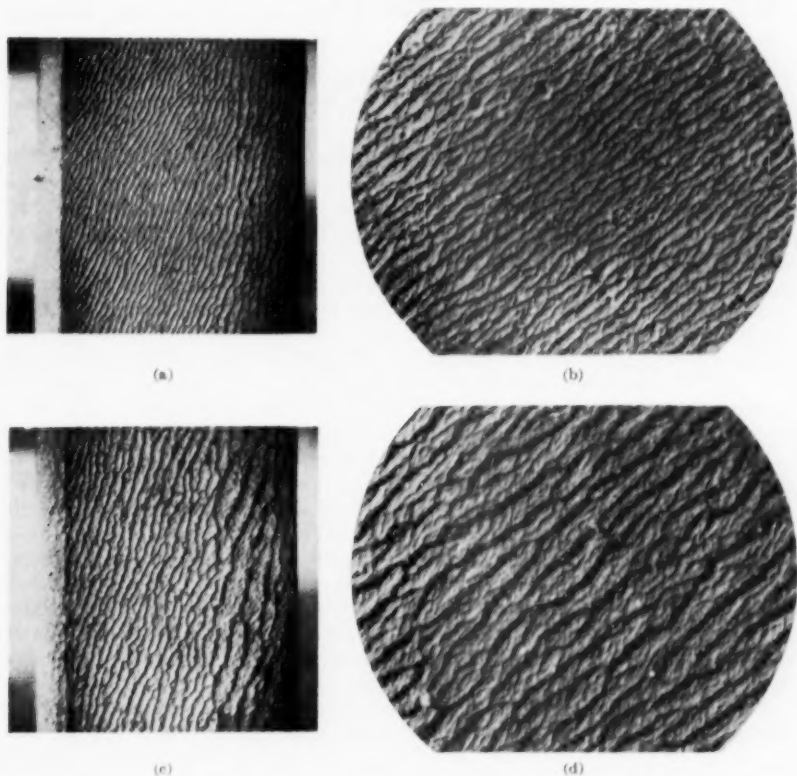


Fig. 5.—Comparison of abrasion patterns on Akron samples (a and c) and on a tire (b and d). Natural rubber. HAF content: a and b, 45; C, 30; D, 25. Magnification: a and c, 3.3 X; b and d, 16 X.

the black-loading affects the surface condition in an analogous manner in the laboratory and on the road. The agreement between Akron machine and road tests is not confined to the qualitative observations illustrated by Figure 5, but preliminary measurements have shown a relatively close correlation between abrasion on the Akron machine and these road tests.

It must again be stressed that this is an exceptional case and that, in general, intrinsic abrasion and contributions of the abrasion pattern must be taken into account separately in the calculations. It is interesting, in this connection, to compare the success of the Lambourn machine in England and in the United

States. Powell and Gough¹⁴ found good correlation between their instrument and road tests, whereas Adams, Reynolds, Messer, and Howland¹⁵ obtained correlation with the road test figures of any two compounds only if they compared them with half the differences in laboratory abrasions.

REFERENCES

- ¹ Schallamach, *Trans. Inst. Rubber Ind.* **28**, 256 (1952).
- ² Fromm, *Ber. 140 der Lilienthalgesellschaft*, 1941.
- ³ Schlippe, *Ber. 140 der Lilienthalgesellschaft*, 1941.
- ⁴ Temple, quoted in "The Mechanical Characteristic of Pneumatic Tires", by Hadekel, Ministry of Supply, London.
- ⁵ Turner, D. M., private communication.
- ⁶ Schallamach, *Proc. Phys. Soc.* **67B**, 883 (1954).
- ⁷ Mandel, Steel, and Stuehler, *Ind. Eng. Chem.* **43**, 2901 (1951); De Decker, Houwink, and van Amerongen, *Proc. Third Rubber Technol. Conf. London*, 1954, p. 749.
- ⁸ Buist, Newton, and Thornley, *Trans. Inst. Rubber Ind.* **26**, 288 (1950); Biard and Svetlik, *India Rubber World* **127**, 363 (1952); Amon and Dannenberg, *Rubber World* **131**, 627, 771 (1955).
- ⁹ Schallamach, *Trans. Inst. Rubber Ind.* **28**, 256 (1952); *Proc. Phys. Soc.* **67B**, 883 (1954).
- ¹⁰ Schallamach, *Trans. Inst. Rubber Ind.* **28**, 256 (1952); Kern, *Kautschuk u. Gummi* **6**, WT 178 (1953); Gough, Hardman, and McLaren, *Trans. Inst. Rubber Ind.* **32**, 27 (1956).
- ¹¹ Schallamach, *J. Polymer Sci.* **9**, 385 (1952).
- ¹² Mullins, *J. Rubber Research* **16**, 275 (1947).
- ¹³ Schallamach, *Proc. Phys. Soc.* **66B**, 817 (1953).
- ¹⁴ Powell and Gough, *Proc. Third Rubber Technol. Conf. London*, 1954, p. 460.
- ¹⁵ Adams, Reynolds, Messer, and Howland, *RUBBER CHEM. AND TECHNOL.* **25**, 191 (1952).

CALORIFIC AND THERMAL PROPERTIES OF NATURAL RUBBER IN THE ORIENTED AND NON-ORIENTED STATES *

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The structural characteristics of high polymers and the sharp dependence of their properties on the physical state create a need for a detailed study of these materials in the region where their physical state undergoes a qualitative change. Besides, a study of the phase transitions of high polymers which crystallize is of independent interest.

The study of the transition of natural rubber from the oriented crystalline state to the non-oriented amorphous state was the problem of this work. The determination of calorific and thermal properties in the transition region was adopted as the method of investigation. It should be noted that, for rubbers, these properties have been studied to a much lesser extent than have the other thermodynamic properties, particularly the mechanical properties.

In order to obtain crystalline rubber, strips of smoked sheet were subjected to repeated rapid stretching at 50°, followed by cooling of the stretched samples to 12–14° C. The stress applied to the rubber during stretching overcomes the deorienting effect of the thermal motion, which impedes the crystallization of non-deformed rubber. At the same time, the heating employed promotes a more complete straightening of the chains since, during heating, intermolecular action diminishes and the chaotically-grouped oriented portions of the macromolecules present in the samples are disrupted. Rapid cooling of the oriented rubber, obtained under such conditions, to temperatures below the melting point of the crystals which formed led to the preservation of the physical state, which was distinguished by an increase of the crystalline phase content, and by a higher degree of orientation, compared with the state of rubber crystallized during the same time by lowering the temperature without stretching. On an average, the extent of stretching amounted to 1400 per cent of the original length.

The oriented rubber was not a highly elastic substance or rubber in the current sense of the word¹. For this rubber, the equilibrium state at room temperature is the crystalline state, which is attested to by the density increase and by the rise of the intensity of crystalline interferences on x-ray photographs of the samples, with an increase of the time of storage. With an increase of temperature, the oriented rubber is converted to the amorphous state, with the highly elastic properties inherent to rubber in this state.

For rubber in these two states—oriented and non-oriented—we measured the heat capacity c_p , the coefficient of thermal expansion α , and the coefficient of isothermal compressibility χ in a temperature range from 20° to 50°. The

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by Gladys S. Macy from *Doklady Akademii Nauk SSSR*, Vol. 95, No. 3, pages 571–574 (1954).

heat capacity at constant volume c_v was calculated from the resulting data from the well-known thermodynamic relationship.

The heat capacity was measured by means of an adiabatic calorimeter², which, very essential for rubbers, had a low thermal conductivity. The absence of heat exchange with the surrounding medium assured temperature equality of the calorimeter and jacket within an accuracy of about 0.0005°. Electrical energy was supplied to the calorimeter heater in increments such that the temperature rise during the experiment amounted to about 1°, so that the corresponding heat capacity value was the average for an interval no greater than 1°. The temperature change was observed with a Beckmann thermometer mounted in the calorimeter jacket. The quantity of electrical energy consumed by heating was measured by the compensation method. The method guaranteed the obtainment of results with an accuracy of about 1 per cent at room temperature, and about 5 per cent at elevated temperatures. The dilatometric method was used for a study of the temperature dependence of the volume. A study of the dependence of volume on pressure was made with a piezometer. The dilatometer and piezometer were filled in vacuo with mercury. The initial volume of the rubber-mercury system was determined

TABLE I

	Oriented rubber	Non-oriented rubber
c_p , cal./g.-deg.	0.479	0.419
α , deg. ⁻¹ ·10 ⁴	76	67
χ , atm. ⁻¹ ·10 ⁴	17.3	5.5
v , ml./g.	1.0682	1.0893
c_v , cal./g.-deg.	0.469	0.352

from their specific gravities at 20° C. In the experiments, the temperature fluctuation did not exceed 0.02° C. Experiments were carried out continuously over the entire temperature range for the study of the temperature dependence of the properties.

The results obtained for the properties of oriented and non-oriented rubber at 20° C are cited in Table I.

The quantities which characterize the properties of oriented rubber are larger in absolute values than those of non-oriented rubber. This elevation should be attributed to disorientation phenomena. It is known that, in partially crystallized oriented rubber, the chains, by means of some of their parts, enter into the composition of the crystallites, and other parts form the amorphous intercrystalline substance. With the relatively rapid temperature rise or pressure reduction which occurs in the experiments for the determination of the properties, a splitting off of links from the crystallites and their conversion to the amorphous state occurs. During these temperature and pressure changes, the process is associated with an additional increase of the total internal energy and volume and with correspondingly large absolute values of c_p , α , and χ for oriented rubber.

Up to temperatures of about 25°, the c_p , α , and χ values are reproduced independently of the direction of the temperature change, which indicates the reversible nature of disorientation, and at the same time indicates that, in the crystallites, at least in a certain portion of them, the interaction forces are small. This instability, an unusual sensitivity to thermal and mechanical effects, indicates an imperfection or structural defect³ and is specific for rubber crystals.

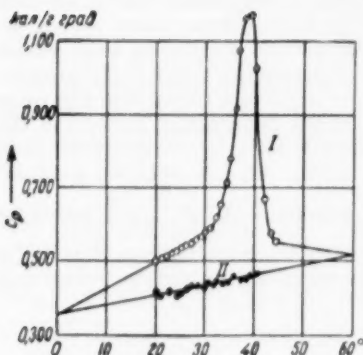


FIG. 1.—Heat capacity c_p of natural rubber in relation to the temperature. I. Oriented rubber. II. Non-oriented rubber. The ordinate indicates the cal./g.-degree; the abscissa the temperature.

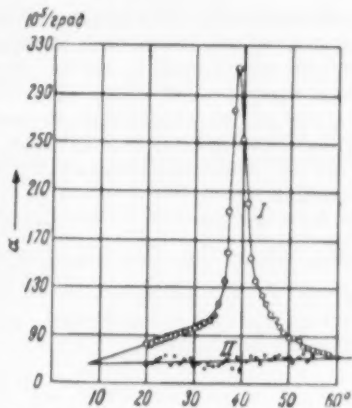


FIG. 2.—Coefficient of thermal expansion α of natural rubber in relation to the temperature. I. Oriented rubber. II. Non-oriented rubber. The ordinate indicates the expansion in $10^{-5}/\text{degree}$; the abscissa the temperature.

The results of the measurements of c_p , α , and χ at higher temperatures are presented in Figures 1–3. The temperature dependence of c_p is shown in Figure 4. From the figures it is evident that, for oriented rubber, the temperature dependence curves of the properties are extremely anomalous. The anomalous increases of the heat capacity and of the coefficients of expansion and of compressibility indicate that, on heating oriented rubber, amorphization occurs, the rate of which increases in a temperature range from 20° to 39° C. With a further increase of temperature, the decrease of the coefficients which was observed indicates the completion of amorphization.

The changes of the heat content and volume during the phase transitions, which occur in a widened temperature interval, were determined from the anomalous values of the heat capacity and coefficient of expansion by integrals, along the width of the temperature interval in which the anomalies of these

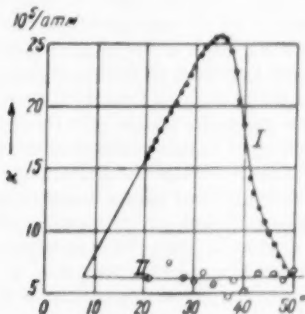


FIG. 3.—Coefficient of compressibility χ of natural rubber in relation to the temperature. I. Oriented rubber. II. Non-oriented rubber. The ordinate indicates the χ value in $10^{-5}/\text{atm}$; the abscissa the temperature.

coefficients occur. By extrapolation of the $c_p = f(t)$ and $\alpha = \varphi(t)$ curves for oriented rubber, before their merging with the corresponding curves for non-oriented rubber, and, by measurement of the areas between these curves, we found that $Q = 7.95$ cal./g. and $\Delta v = 0.020$ ml./g. Employing these values of Q and Δv , we calculated the dependence of the melting point on the pressure by the Clausius-Clapeyron equation. Moreover, it was shown that the value of dT/dP does not depend on the width of the temperature interval in the transition region, but amounts to approximately 0.02 deg./megabar, for both the total interval and for individual steps of it. We also obtained a dT/dP

value close to this from the Ehrenfest equation, $dT/dP = \frac{Tv \cdot \Delta\alpha}{\Delta c_p}$, where $\Delta\alpha$ and Δc_p are the differences of the values of the corresponding coefficients for oriented and non-oriented rubber at 39° C, where the anomalous values pass through a maximum.

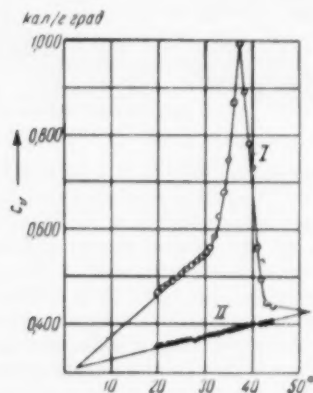


Fig. 4.—Heat capacity c_p of natural rubber in relation to the temperature. I. Oriented rubber. II. Non-oriented rubber. The ordinate indicates the c_p value in cal./g.-degree; the abscissa the temperature.

The crystalline phase content in oriented rubber, calculated from the density, amounts to about 24 per cent. On conversion to completely crystalline rubber, the results which we obtained for the change of the thermodynamic quantities⁴ amounted to 34 cal./g. for the heat of fusion and 0.089 ml./g. for the volume change. The melting point and heat of fusion of rubber were abnormally low compared with the values which may be expected, proceeding from the dependence of these quantities on the molecular weight for low-molecular compounds. The unusual phase transition of natural rubber consists more in the fact that, in this transition, it is as if there occurs a simultaneous appearance of the regularities inherent to different types of phase transitions in low-molecular substances. Thus, if the fusion of each given member of the crystals represents a phase transition of the first kind, then the macrotransition of oriented rubber to non-oriented rubber, with respect to the nature of the change of properties in the transition region, suggests a phase transition of the second kind. Moreover, the temperature interval of the transition, the origin of which was interpreted for polymers for the first time by Aleksandrov⁵, and in which anomalous c_p , α , χ and c_v values were observed, may be considered as the critical region,

according to concepts Semenchko⁶ developed concerning the identity of the critical phenomena and phase transitions of the second kind.

ACKNOWLEDGMENTS

We express sincere appreciation to V. V. Tarasov for the suggestion of the subject and for guidance of the work, and also to V. A. Kargin, B. A. Dogadkin, and G. L. Slonimsky for discussion of the results of the work.

REFERENCES

- ¹ The mechanical properties of oriented rubber are characterized by the following values: Young's modulus of approximately 9000 kg./sq. cm. and tensile strength of 800 kg./sq. cm. at a relative elongation of 70 per cent.
- ² Skuratov, *Kollod. Zhur.* **9**, 133 (1947).
- ³ Kargin and Markova, *Zhur. Fiz. Khim.* **27**, 1236 (1953).
- ⁴ These values for oriented rubber exceed those available in the literature (Bartenev, *Zhur. Tekh. Fiz.* **22**, 426 (1952); Boonstra, *RUBBER CHEM. AND TECHNOL.* **24**, 845 (1951)) for both raw rubber and for the vulcanizate.
- ⁵ Aleksandrov, Transactions of the 1st and 2nd Conferences on High-Molecular Compounds, *Akad. Nauk SSSR Press*, 1945.
- ⁶ Semenchko, *Zhur. Fiz. Khim.* **26**, 1337 (1952).

CRYSTALLIZATION IN NATURAL RUBBER. IV. TEMPERATURE DEPENDENCE *

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INTRODUCTION

Considerable experimental work on the crystallization of unstrained natural rubber, both vulcanized and unvulcanized, has been described previously¹. The rate of crystallization of raw rubber increases as the temperature at which the crystallization occurs is reduced, until a maximum value is attained at about -26°C . On lowering the temperature further, the rate decreases continuously. A similar temperature dependence is found for vulcanized rubber, although the rate at any given temperature is lower.

Small quantities of certain impurities, for example, stearic acid, greatly increase the rate of crystallization of raw rubber². Such impurities are normally present in plantation smoked-sheet rubber, on which many of the reported measurements of rates of crystallization have been made. The measurements now reported have, therefore, been made with a purified rubber (deproteinized pale crepe) containing negligible quantities of the relevant impurities. Peroxide vulcanizates prepared from such a rubber have also been examined.

The crystallization process was followed dilatometrically³.

THEORETICAL TREATMENT

TIME FUNCTIONS GOVERNING THE CRYSTALLIZATION PROCESS

In a previous publication⁴ it was shown that the volume changes accompanying crystallization in vulcanized natural rubber at -26°C may be described to a first approximation by time functions of the Avrami type⁵. These relations, obtained from statistical considerations, give the amount of material C transformed to a new phase after a time t when nuclei of the new phase appear randomly in space and then grow in certain simple spacial forms at a constant rate. If the growing units are spherulites or polyhedral clusters of many small crystals containing a constant fraction A of crystalline material within the growing spherulite, two extreme time functions may be obtained, corresponding to two limiting conditions of nucleus formation:

(1) When all the crystal nuclei are present initially, none being formed during the course of the crystallization process, the degree of crystallization is given by:

$$C = A[1 - \exp\{-\frac{4}{3}\pi R^3 K t^3\}] \quad (1)$$

where K is the average number of nuclei per cc. and R is the rate of growth of the radius of the spherulite.

* Reprinted from the *Journal of Polymer Science*, Vol. 18, pages 321-334 (1955).

(2) When crystal nuclei appear at an average rate K' per cc. per second throughout the crystallization process, the corresponding relation is found to be:

$$C = A[1 - \exp\{-(\pi/3)R^3K'/t\}] \quad (2)$$

The corresponding times at which half of the equilibrium degree of crystallization is attained are given by:

$$\ln \tau_1 = -\frac{1}{3} \ln [(4/3)\pi R^3K'/\ln 2] \quad (3)$$

and

$$\ln \tau_2 = -\frac{1}{3} \ln [(\pi/3)R^3K'/\ln 2] \quad (4)$$

respectively.

TEMPERATURE DEPENDENCE

A relation for the temperature dependence of the rate of formation of nuclei may be obtained from classical nucleation theory⁶. The formation of a crystal nucleus, treated as a small sphere of radius r , is accompanied by a free energy change ΔF which may be considered to comprise two parts. The first is that due to the free energy of fusion, and is proportional to the volume of the nucleus; the second, of opposite sign, is that required to form the crystalline-amorphous boundary, and is proportional to the surface area of the nucleus. The nucleus radius r^* giving a maximum value of the resultant free-energy change may be considered a critical radius, since nuclei formed spontaneously having a smaller radius tend to disappear, while those formed having a larger radius will tend to grow.

The critical radius is found² to be:

$$r^* = 2\sigma T_M(T_M - T)^{-1}h_f^{-1} \quad (5)$$

where σ is the free energy of formation of the crystalline-amorphous surface, per sq. cm., and h_f is the latent heat of fusion per unit volume of the crystalline phase. T_M is the equilibrium melting temperature and T is the temperature at which the formation of nuclei occurs. The corresponding value for the free energy of formation of a nucleus of the critical size is given⁷ by:

$$\Delta F^* = \frac{16}{3}\pi\sigma^3T_M(T_M - T)^{-2}h_f^{-2} \quad (6)$$

The rate of formation of nuclei of the critical size by the fortuitous aggregation of chain segments is then given⁸ by a relation of the form:

$$K' = \bar{K}' \exp\{-\Delta U/kT\} \exp\{-\Delta F^*/kT\} \quad (7)$$

where \bar{K}' is a constant, k is Boltzmann's constant, and ΔU is the activation energy governing the transport of amorphous material to a nucleation site by thermal fluctuations. The rate of growth of a nucleus larger than the critical size at temperatures well below the equilibrium melting temperature will be limited only by the rate at which amorphous material approaches the nucleus surface; the corresponding temperature dependence of the rate of growth R of the crystal radius is, therefore, given by:

$$R = \bar{R} \exp\{-\Delta U/kT\} \quad (8)$$

where \bar{R} is a temperature-independent parameter. On substituting in Equation (2) for K' and R from Equations (7) and (8), respectively, the half-life of the crystallization process is obtained as a function of temperature.

The experimentally inaccessible quantity ΔU may be obtained as a function of the temperature T_1 at which the rate of crystallization is a maximum, by equating to zero the derivative with respect to the temperature of the crystallization half-life. The relation so found is:

$$\Delta U = 4/3\pi\sigma^2 T_M^2 (3T_1 - T_M)(T_M - T_1)^{-2} h_f^{-2} \quad (9)$$

The corresponding relation for the half-life of crystallization as a function of temperature is:

$$\ln \tau_{1/2} = B + \alpha \cdot \beta(T) \cdot \sigma^3 \quad (10)$$

where:

$$\alpha = 4/\pi T_M^2 h_f^{-2} k^{-1} \quad (11)$$

$$\beta(T) = [(3T_1 - T_M)(T_M - T_1)^{-2} + (T_M - T)^{-2}] T^{-1} \quad (12)$$

and B is a constant containing \bar{K}' and \bar{R} .

Values for the constant α and the function $\beta(T)$ at each temperature may be obtained from given values of the heat of fusion h_f , the equilibrium melting temperature T_M , and the temperature T_1 at which crystallization is most rapid. In applying Equation (10) in a later section, the heat of fusion⁸ has been taken as 6.4×10^6 ergs/g., and the equilibrium melting temperature as 30°C . This is somewhat higher than the recently determined figure⁹ of $28 \pm 1^\circ \text{C}$, but the method of measurement there used is likely to underestimate the equilibrium value, possibly by two or three degrees. The temperature of most rapid crystallization has been taken as -24°C , as indicated by the experimental results on the purified rubber described in a subsequent section.

EFFECT OF THE INTRODUCTION OF CROSS-LINKS

The decrease of the final extent of crystallization caused by the introduction of cross-links has been ascribed in a previous publication⁴ to the steric prohibition of crystallization in an elementary volume V_1 around each cross-link. If they are randomly distributed, of number per cc., or density, n , the equilibrium degree of crystallization is given by:

$$A_n = A_0 \exp\{-nV_1\} \quad (13)$$

from statistical considerations.

The retardation of crystallization in the presence of cross-links has been attributed⁴ to the prohibition of crystal nucleus formation within a volume V_2 around each cross-link. The prohibited volume may be considered to arise partly from steric prohibition and partly from the finite size of an effective crystal nucleus. If the sterically prohibited volume V_1 and the critical size of the crystal nucleus are both assumed to be spherical, of radius r_1 and r^* , respectively, the volume V_2 prohibited to the centers of nuclei around each cross-link is given by:

$$V_2 = \frac{4}{3} \pi (r_1 + r^*)^3 \quad (14)$$

The rate of nucleus formation is then given by a relation analogous to Equation (13):

$$K'_n = K'_0 \exp\{-nV_2\} \quad (15)$$

and the crystallization half-life is obtained from Equations (4) and (15) in the form:

$$(\ln \tau_1)_n = (\ln \tau_1)_0 + nV_2/4 \quad (16)$$

It is also possible that the rate at which amorphous material approaches a nucleation site is reduced by the introduction of cross-links. If this is so, the rate of crystallization will be decreased to a greater extent than is predicted by Equation (16).

Flory⁹ has shown, in a thermodynamic study of crystallization in high polymers, that the introduction of cross-links cause a reduction in the equilibrium melting temperature. A third cause of retardation might therefore be inferred, since the corresponding increase of the free energy of formation of a nucleus of the critical size results in a reduced rate of nucleation. It is shown in the Appendix, however, that this rate-reducing mechanism is equivalent to the proposed prohibition of nucleus formation around each cross-link.

EXPERIMENTAL METHOD

PREPARATION OF THE TEST-PIECES

The unvulcanized rubbers examined were plantation smoked-sheet rubber and a purified crepe rubber described previously² as deproteinized crepe. Test-pieces in the form of rods 10 cm. long and of square cross-section of approximately 4 mm. side were wrapped in stainless-steel gauze and sealed into the bulbs of glass dilatometers, which were subsequently filled with mercury. The peroxide vulcanizates (in the form of many irregularly shaped pieces having dimensions of about 5 by 5 mm. by 1 to 2 mm.) were prepared and characterized as described in the Appendix from the purified rubber.

A conditioning treatment, as described previously², was imposed in all cases. The filled dilatometers were heated for 1 hour at a temperature of 100° C, and then kept for about 16 hours at 21° C. After this treatment, the dilatometers were placed in a refrigerated chamber held at a fixed temperature in the range -37 to 0° C. Large initial thermal contractions took place, which were virtually complete in 5 minutes. Thereafter slow decreases of volume took place, which are ascribed to crystallization. The course of the volume contraction was found to be reproducible when the conditioning treatment was freshly imposed before each recrystallization, and the same samples were, therefore, examined at each crystallization temperature.

CHARACTERIZATION OF THE CRYSTALLIZATION PROCESS

Time functions of the form given in Equations (1) and (2) were found to describe the volume contractions to a first approximation. In the later stages of crystallization, however, substantial departures from the theoretical course occurred, the experimentally observed decreases of volume being more protracted than the theoretical relations suggest. Also no true equilibrium was attained in the course of the experiments, the volume progressively decreasing over long intervals of time. Similar secondary crystallization processes have been noted in the crystallization of polyethylene terephthalate¹⁰, polyethylene¹¹,

and polyhexamethylene adipamide¹². The relative magnitude of the secondary crystallization in natural rubber over the temperature range employed is shown in the typical curve of volume contraction as a function of time given in Figure 1.

It is clear that the value obtained from such a curve for the time at which half of the primary crystallization has occurred will be insensitive to the particular value chosen for the equilibrium degree of crystallization, and the half-life has been used hereafter to characterize the rate of crystallization without qualification. It is necessary, however, to define the volume contraction specified as the completion of the primary crystallization process. This has been taken arbitrarily as the volume contraction that has occurred at a time of twice the half-life. After such a time interval processes following the time functions given in Equations (1) and (2) would be essentially complete. Also, the values so obtained are approximately those obtained from the intersection of the linear

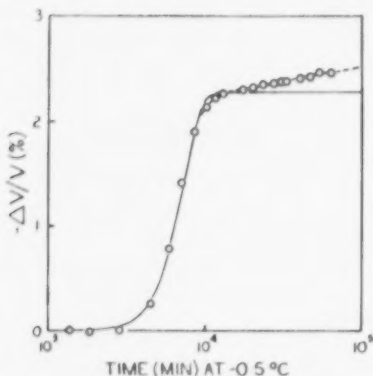


Fig. 1.—The progress of crystallization in the purified rubber at -0.5°C . The full curve is of the form given by Equation (2).

approximations to the steep part of the primary crystallization and the secondary crystallization on a logarithmic time plot, which is an alternative method of characterizing the extent of the primary crystallization. Finally, using values for the quasi-equilibrium volume change so obtained, and the half-life, a relation calculated from either Equation (1) or Equation (2) was found to describe successfully the major part of the crystallization process. The full curve of Figure 1 was obtained in this way from Equation (2).

EXPERIMENTAL RESULTS: PURIFIED RUBBER

The time dependence of the volume contraction was found to be that predicted by Equation (2) to a first approximation at each of the crystallization temperatures employed, suggesting the growth of spherical crystal structures from nuclei which appear at a constant rate. The experimentally determined half-lives are plotted against the crystallization temperatures in Figure 2, and the rate of crystallization is seen to be most rapid at a temperature of about -24°C .

In considering the applicability of classical nucleation theory to the temperature dependence of the crystallization rate for natural rubber, only those

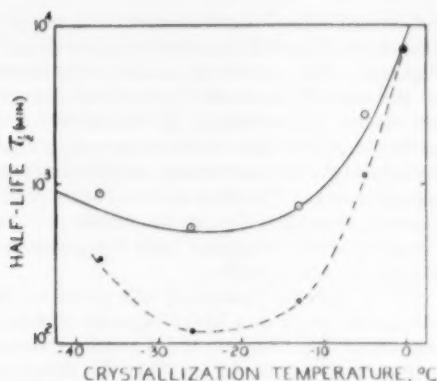


Fig. 2.—Dependence of the half-life of crystallization on the crystallization temperature for purified rubber, open circles, and smoked sheet rubber, filled in circles. The full curve is of the form given by Equation (10).

measurements where no foreign nucleating sources are present are relevant. The measurements on the purified rubber appear satisfactory in this respect, since (1) further purification by extraction with acetone was found not to alter the crystallization behavior appreciably, and (2) the time functions characterizing the crystallization process indicate the formation of nuclei at a constant rate, a behavior which might be expected for the pure polymer.

In Figure 3, the half-lives of the crystallization process for the purified rubber are plotted on a logarithmic scale against the temperature function $\beta(T)$ defined by Equation (12). A linear relation is seen to characterize the experimental points approximately, in accordance with Equation (10). From the slope of the linear relation a value for σ , the free energy of formation of the crystalline-amorphous interface, may be obtained, and is found to be 6.3 ergs/cm.². Values for other crystallizing polymers have been reported of a similar magnitude¹². Using the value obtained for σ , the activation energy ΔU for material transport may be calculated from Equation (9), and is found to be 10 kcal./g.-mole. Similar values have been obtained¹⁴ for the activation energy of viscous flow in natural rubber, which is a comparable process.

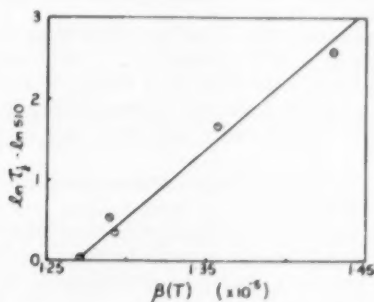


Fig. 3.—Dependence of the crystallization half-life on the calculated temperature function, $\beta(T)$.

The variation of the half-life of crystallization with temperature corresponding to the linear relation of Figure 3 has been calculated, and is represented by the full curve of Figure 2. The agreement between the experimental points for the purified rubber and the full curve of Figure 2 is a measure of the success of classical nucleation theory in describing the temperature dependence of the crystallization rate for natural rubber over the present temperature range.

In Figure 4, the quasi-equilibrium volume contraction is plotted against the temperature of crystallization. The final volume contraction is seen to be lower at lower temperatures of crystallization for the purified rubber, and, within the rather large experimental error associated with this measurement, an approximately linear relation is found to hold.

An increased rate of nucleus formation compared to the rate of crystal growth would presumably result in a lower ultimate degree of crystallization, since an amorphous zone would be required between a growing crystal and each stable nucleus it encountered to make possible the fitting of interconnecting chains. It seems reasonable to assume that the rate of nucleus formation is

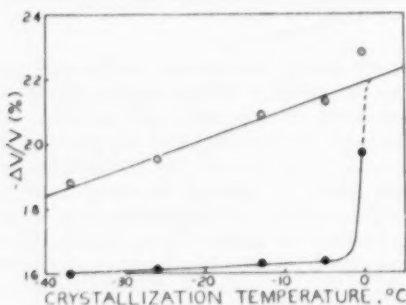


FIG. 4.—Effect of the crystallization temperature on the final volume contraction for purified rubber, open circles, and smoked-sheet rubber, filled-in circles.

relatively increased at lower temperatures, and some reduction in the degree of crystallization attained might, therefore, be expected on lowering the crystallization temperature.

EXPERIMENTAL RESULTS: CROSS-LINKED PURIFIED RUBBER

The volume contractions were found to follow time functions of the form given in Equation (2) to a first approximation, indicating spherical crystal growth patterns from nuclei appearing at a constant rate. The introduction of cross-links was found to decrease the quasi-equilibrium volume contraction and markedly retard the crystallization process at each crystallization temperature¹⁵.

The final volume contraction attained at a temperature of -26°C was found to decrease with increasing density of cross-linking, according to an approximately linear relationship⁴. If this relationship is assumed to be that predicted by Equation (13) for small degrees of cross-linking, a value may be obtained from the slope for the volume V_1 sterically prohibited to crystallization by each cross-link⁴. The value so found was:

$$V_1 = 5.1 \times 10^{-21} \text{ cm}^3$$

This value may be an underestimate of the true prohibited volume. If the introduction of cross-links reduces the rate of nucleus formation compared to the rate of crystal growth, there will be fewer crystal-nucleus interferences, and the volume contraction will be larger than would be attained under constant nucleation conditions. It is difficult to assess the extent to which this effect compensates the excluded volume effect due to cross-links. In a more refined theoretical treatment, it will be necessary to modify Equation (13) appropriately.

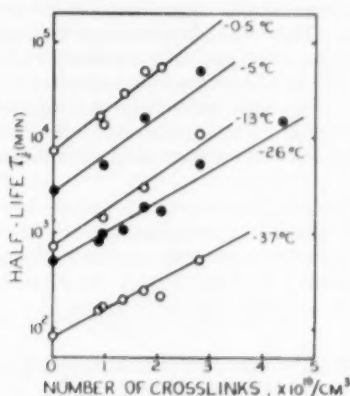


Fig. 5.—Experimental relations between the crystallization half-life and the degree of cross-linking at the various crystallization temperatures. Note that the experimental relation obtained at -37°C is displaced vertically downward by one decade for clarity of display.

No major influence of the temperature at which crystallization was effected on the prohibited volume was shown by the experimental measurements at other temperatures. The observations were, however, insufficiently accurate to reveal small changes.

The experimentally determined half-lives of crystallization for the cross-linked rubbers are plotted in Figure 5 on a logarithmic scale against the number of cross-links per cc. The experimental points are seen to be described approximately by linear relations, as predicted by Equation (16). The retard-

TABLE I

Crystallization temp. ($^{\circ}\text{C}$)	-37	-26	-13	-5	-0.5
$(\partial \ln \tau_1 / \partial n) \times 10^{-30} \text{ cc.}$	7.0	7.5	8.7	9.2	10.0
$V_2/4 \times 10^{-30} \text{ cc.}$	0.8	1.0	1.6	2.2	2.9

ation of crystallization at each temperature caused by the introduction of cross-links may be characterized by the slope:

$$(\partial \ln \tau_1 / \partial n)$$

of the corresponding linear relation of Figure 5. The experimental values are given in Table I for the various temperatures employed.

The retardation arising from the prohibition of crystal nucleus formation in a region surrounding each cross-link is predicted by Equation (16) to be given by $V_2/4$. The magnitude of this quantity may be calculated from Equation (14) when values of τ_1 and τ^* are known. The value of τ_1 may be obtained from

the experimentally determined value of V_1 given above, and values of r^* may be calculated at each temperature from Equation (5), using the value for σ obtained in a previous section. In this way the values of the quantity $V_2/4$ given in Table I were obtained.

The calculated values of $V_2/4$ are seen in Table I to be of the same order as the experimentally observed retardations, although considerably smaller. However, the calculated values of $V_2/4$ are essentially minimum estimates for two reasons. First, as described above, the value obtained for the sterically prohibited volume V_1 around each cross-link may be an underestimate of the true prohibited volume. The value of r_1 is correspondingly uncertain. Second, the critical nucleus size and the sterically prohibited volume have both been assumed spherical in order to obtain a simple relation for the volume V_2 banned to nucleus formation. In general, both these volumes will be of more complex form, and the corresponding volume excluded to the centers of nuclei may be considerably larger than the value obtained by considering equivalent spherical volumes.

Even when such correcting factors are included, it seems unlikely that the major part of the retardation of crystallization occasioned by cross-linking will be accounted for by a nucleus-excluded volume mechanism, especially at low crystallization temperatures, and significant contributions to the retardation due to reduced segment mobility may be inferred.

EXPERIMENTAL RESULTS: THE INFLUENCE OF IMPURITIES

The time dependence of the volume contraction of plantation smoked-sheet rubber was found to be that predicted by Equation (2) to a first approximation at the highest temperature employed: -0.5°C . At lower temperatures, better agreement was obtained with a time function of the form given in Equation (1), indicating spherical crystal growth from nuclei which are effectively all present at an early stage in the crystallization process. The smoked-sheet rubber was also found to crystallize much more rapidly than the purified rubber at temperatures below -0.5°C , as shown in Figure 2.

Presumably the crystallization-accelerating impurities present in smoked-sheet rubber are precipitated locally at temperatures below -0.5°C , and catalyze the crystallization of the rubber. Larger quantities of the relevant impurities might be expected to precipitate at still higher temperatures. It was found that the addition of 2 per cent stearic acid to the smoked-sheet rubber cause a marked acceleration of the crystallization process at -0.5°C , the half-life being decreased from about 7000 to 1500 minutes.

Measurements were made of the rate of crystallization at a temperature of -26°C of vulcanized rubbers, with and without crystallization-promoting impurities present. The test-pieces were prepared from smoked-sheet rubber containing 2 per cent by weight of *tert*-butyl perbenzoate by heating for 50 minutes at a temperature of 140°C . The half-life of crystallization of these was found to be 1500 minutes, which increased to 2600 minutes after extraction with acetone. Similar differences were found between nominally identical vulcanizates prepared from the smoked-sheet rubber and the purified rubber. It appears therefore that, although the crystallization-promoting impurities are still active under these conditions, their efficiency is much reduced, since the factor by which the rate is increased is somewhat less than 2, compared to a factor of about 4 for unvulcanized rubber. Moreover, similar vulcanizates pre-

pared from smoked-sheet rubber having 1 per cent by weight of stearic acid added, initially transparent, became opaque on standing at room temperature due to the formation of a bloom on the surface. It seems probable that the impurities are hindered from precipitating locally in a cross-linked rubber, and consequently tend to diffuse to the surface to be deposited there.

The values obtained for the quasi-equilibrium volume contraction of the smoked-sheet rubber are plotted in Figure 4 against the crystallization temperature. They are seen to be lower than those found for the purified rubber at temperatures where the crystallization-promoting impurities are effective, and to exhibit a much smaller temperature dependence. It was proposed previously² that the relevant impurities act by facilitating crystal nucleus formation. The curve of Figure 4 for smoked-sheet rubber is that to be expected when a specific nucleation mechanism becomes operative below a certain temperature, and the resulting greatly increased number of crystal-nucleus interferences causes a reduction of the final volume contraction. The lowered degree of crystallization will thereafter be largely temperature-insensitive, as is found experimentally, since the number of crystal nuclei present is governed mainly by the disposition of precipitated impurities rather than the probability of the formation of a critical size, which is temperature dependent, by fortuitous aggregation.

GENERAL CONCLUSIONS

The experimental measurements of the rate of crystallization for the deproteinized crepe rubber at various temperatures have been shown to be described adequately by classical nucleation theory. This is at first sight surprising. It has recently been shown¹³, however, that a free-energy function for nucleus formation not essentially dissimilar to that required by classical theory can be derived for high polymers from the lattice treatment of polymer crystallization⁹. Values have been derived from the experimental results for the free-energy of formation of the crystalline-amorphous interface and the activation energy governing the motion of chain segments.

The influence of cross-linking in retarding crystallization has been shown to be considerably greater than is predicted by an elementary banned volume mechanism, and is therefore ascribed in part to the reduction of the mobility of chain segments occasioned by cross-linking.

The influence of naturally occurring impurities in smoked-sheet rubber in accelerating crystallization has been examined further. It appears that at sufficiently high temperatures they are ineffective, presumably because they are precipitated too slowly to appreciably affect the crystallization process. Their efficiency is also reduced in vulcanized rubber, apparently because they are precipitated with difficulty within the rubber network.

ACKNOWLEDGMENTS

This work forms part of a program of research undertaken by the Board of the British Rubber Producers' Research Association. The samples of peroxide cross-linked rubber were provided by C. G. Moore and W. F. Watson of these laboratories. A brief description of the preparation and characterization is given in the Appendix. The purified pale crepe rubber was kindly provided by G. J. van der Bie of the Indonesian Rubber Research Institute.

APPENDIX

REDUCTION IN MELTING TEMPERATURE CAUSED
BY CROSS-LINKING

Flory² has shown that the equilibrium melting temperature T_M is reduced to T'_M by the incorporation of n cross-links per cc., where T'_M is given by:

$$(T'_M)^{-1} - (T_M)^{-1} = [-\ln(1-X) - \mu'X^2]Nk\rho/(h_f I) \quad (17)$$

where μ' is a constant and X is the "mole" fraction of cross-links, given by:

$$X = nI/(N\rho)$$

I is the molecular weight of the crystallizing structural unit, here assumed to be the isoprene unit, N is Avogadro's number and ρ is the density, assumed equal in the crystalline and amorphous phases. When the degree of cross-linking is small, Equation (17) may be approximated by:

$$T'_M = T_M - T_M^2 nk/h_f \quad (18)$$

The free energy ΔF^* of formation of a crystal nucleus of the critical size in the cross-linked rubber may be obtained by replacing T_M in Equation (6) by T'_M . Using Equation (18) above, and (5), and assuming that the reduction of melting temperature $T_M - T'_M$ is much smaller than the degree of supercooling $T_M - T$, we obtain:

$$\Delta F^*_n = \Delta F^* + 4/3(r^*)^2 nkT$$

The rate of nucleus formation in the presence of cross-links is, therefore, given by:

$$K'_n = K'_0 \exp\{-4/3\pi(r^*)^2 n\}$$

which is the limiting form of Equation (15) when the cross-links cause a negligible amount of steric prohibition to crystallization, and consist effectively of point discontinuities. The effect of the reduction of the equilibrium melting temperature in retarding nucleus formation is thus seen to be equivalent to the proposed prohibition of nucleus formation due to their finite size, around each cross-link.

PREPARATION AND CHARACTERIZATION OF THE PEROXIDE
VULCANIZATES BY C. G. MOORE AND W. F. WATSON

Samples of dried purified pale crepe rubber were vulcanized *in vacuo* at 120 and 140° C by means of di-*tert*-butyl peroxide. Chemical determinations of the degree of cross-linking of the vulcanizates were made by infrared spectroscopic analysis of the *tert*-butanol and methane formed, with the assumption that:

$$\text{No. of cross-links} = \frac{1}{2} (\text{No. of molecules of } (\text{CH}_3)_2\text{COH} + \text{CH}_4)$$

Full details of the experimental procedure will be given in a forthcoming publication.

SYNOPSIS

Experiments are described in which the temperature dependence of crystallization in natural rubber, unvulcanized and vulcanized by a peroxide, was investigated dilatometrically over the temperature range -37° to 0° C. Avrami-

type time functions describe the progress of crystallization to a first approximation. The numerical parameters indicate the growth of spherical crystal structures from nuclei which appear randomly at a constant rate in a purified rubber. It is shown that classical nucleation theory describes the temperature dependence to a first approximation. The retardation of crystallization caused by the introduction of cross-links is ascribed partly to a reduction of chain segment mobility and partly to the prohibition of crystal nucleus formation around each cross-link. Crystal nucleation appears to be promoted in plantation smoked-sheet rubber by the nonrubber components at temperatures below 0° C.

REFERENCES

- ¹ Bekkedahl and Wood, *Ind. Eng. Chem.*, **33**, 381 (1941); Wood and Bekkedahl, *J. Appl. Phys.*, **17**, 362 (1946); Russell, *Trans. Faraday Soc.*, **47**, 539 (1951).
- ² Gent, *Trans. Inst. Rubber Ind.*, **30**, 139 (1954).
- ³ Bekkedahl and Wood, *Ind. Eng. Chem.*, **33**, 381 (1941).
- ⁴ Gent, *Trans. Faraday Soc.*, **50**, 521 (1954).
- ⁵ Avrami, *J. Chem. Phys.*, **7**, 1103 (1939); **8**, 212 (1940); **9**, 177 (1941).
- ⁶ Frenkel, "Kinetic Theory of Liquids", Oxford Univ. Press, 1946, p. 413.
- ⁷ Frenkel, "Kinetic Theory of Liquids", Oxford Univ. Press, 1946, p. 413; Mandelkern, Quinn, and Flory, *J. Appl. Phys.*, **25**, 830 (1954).
- ⁸ Roberts and Mandelkern, *J. Am. Chem. Soc.*, **77**, 781 (1955).
- ⁹ Flory, *J. Chem. Phys.*, **17**, 223 (1949).
- ¹⁰ Hartley, Lord, and Morgan, *Phil. Trans. Roy. Soc.*, **A247**, 23 (1954).
- ¹¹ Kovacs, International Symposium on Macromolecular Chemistry, Turin, 1954. Available in the United States from Interscience Publishers, Inc.
- ¹² Hartley, Lord, and Morgan. International Symposium on Macromolecular Chemistry, Turin, 1954. Available in the United States from Interscience Publishers, Inc.
- ¹³ Mandelkern, Quinn, and Flory, *J. Appl. Phys.*, **25**, 830 (1954).
- ¹⁴ Smallwood, *J. Appl. Phys.*, **8**, 505 (1937); Saunders and Treloar, *Trans. Inst. Rubber Ind.*, **24**, 92 (1948).
- ¹⁵ Bekkedahl and Wood, *Ind. Eng. Chem.*, **33**, 381 (1941); Russell, *Trans. Faraday Soc.*, **47**, 539 (1951).

OBSERVATIONS ON THE RELATION BETWEEN LABORATORY AND TEST-STAND MEASUREMENTS OF TIRE TREADS AND THEIR BEHAVIOR ON THE ROAD*

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Compounding development requires economical, rapid, and accurate assessment of the qualities prescribed for tire treads with respect to driving safety, abrasion, and dynamic fatigue. Laboratory and test stand measurements are utilized for this as a preselection means prior to road tests. The complex nature of the conditions in practical driving on the road, on the one hand, where the characteristic behavior of the tread is determined by the type of compound, the tire construction, the type of vehicle, and the nature of the road, and on the other hand, the often too great intensity of laboratory and test stand conditions and their lack of similarity, are the causes for difficulties in the correlation of laboratory and test stand results and actual service. With the aid of several examples and comparisons, the importance of the nature and intensity of the treatment in the testing of the above named characteristics of safe travel, abrasion, and dynamic fatigue will be discussed.

INTRODUCTION

In evaluating new developments in tires, road tests are of the greatest importance. These driving tests give the best correlation with practical results obtained by customer and user—briefly called “service” in what follows. To build tires and to test their characteristics with the tires themselves is, therefore, a basic principle which will always be valid in the field of testing techniques. However, the expenditure of material and, above all, of the time required in road tests is so great that the demand for economical, rapid, and accurate methods of evaluation by laboratory and test stand measurements still remains. They should serve as a preselection means for road tests, and, in addition, as a control for the uniformity of the raw materials and for the manufacture. To test economically and rapidly is a demand that is easily met; the real problem is to test accurately, and especially realistically. By this is meant that between the test results and actual service there must be a satisfactorily close correlation in the statistical sense.

It is not possible within the limits of this presentation of the problem to deal with the essential characteristics that are desired in a tire. We propose, therefore, to direct our attention to tire treads and to deal with three properties, namely: (1) driving safety, (2) wear, and (3) dynamic destruction. With the help of several examples we shall discuss the following questions related to these three properties:

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- (a) Why it is so difficult to obtain good correlation, and
- (b) What can be done to improve the correlation?

In this connection, we wish to stress the following three points which hold for the laboratory and test stand measurements and also for road tests:

1. Each of the three characteristics named is a resultant of the type compound, tire construction, type of vehicle, and character of the road.

If, for example, in the measurement one includes only the effect of type of compound, these measurements should not be expected to show a close relationship with the behavior in service.

2. The evaluation of the properties depends markedly on the test conditions; that is, the properties are not to be considered as fixed values but, instead, depend greatly on the test conditions, and, for this reason:

3. A correlation is to be expected only provided the test conditions are adapted in nature and intensity to service requirements. For this, a knowledge of such practical requirements is necessary.

Each of the characteristics will be discussed in a section by itself. Each section will be preceded by a review of the literature, for which, however, no claim of completeness is made, but which represents a purely subjective selection (Table 1). The examples in each section serve to hold constantly before our mind the three points already mentioned: the complex nature, the influence of the test conditions, and conformity to the nature and intensity of service.

DRIVING SAFETY

In view of the high average driving speeds, the question of the way the tire grips the road is one of great importance for safe driving. Good ground gripping is necessary in order to give a tire good traction, good braking power, and good sidewise stability.

A SURVEY OF THE PROBLEM

In order to meet these requirements, measurements were made of the coefficients of friction of tire-tread compounds and of possible ways of increasing the friction. Of the laboratory measuring procedures, only a few, which represent the three characteristic ways of testing, will be mentioned.

Conant, Dum, and Cox¹ and Boonstra² have measured the coefficients of friction directly from the ratio of the force in the direction of sliding to the force at right angles to it, i.e., according to the principle of the inclined plane. We³ in our tests determined the coefficients of friction from the logarithm of the ratio of two measurable forces when a test-strip was passed over a rotating slipping track, according to the principle of the rope brake.

Weinbrenner and Ecker⁴ utilized a turntable (Karussell) method, in which the deflection of a wheel dragged on a circular track caused by the centrifugal force gave a measure of the tendency of the compound to slip. These authors also studied the effect of the type of friction surface and of the temperature on the coefficients of friction.

Wilkinson⁵ investigated the coefficient of friction on ice, and preferred these laboratory measurements to road tests because, in the latter, there can be great deviations in the results; for example, those caused by temperature variations during the measurements. The author observed a strong dependence of the

TABLE I
REVIEW OF LITERATURE ON THE PROPERTIES MEASURED IN EXPERIMENTS
IN LABORATORY, ON TEST STAND, AND ON THE ROAD

Effect of	Compound					Tire construction					Travel conditions					Road conditions				
	Type of rubber, filler, mixing technique					Tread pattern, structure, cord					Air pressure, speed, type vehicle, wheel mounting					Road surface, temperature, weather				
<i>Safety</i>																				
Laboratory	1	2	3	4	5											1	2	3	4	5
Test stand	6	7				6	7				6	7				6	7			
Road	6	7	8	9		6	7	8	9	10	6	7	8	10	11	6	7	8	9	10
											12	13				12	13			11
<i>Wear</i>																				
Laboratory	3	14	15	16	17											3	19	21	22	
Test stand	18	19	20	21	22															
Road	7	24	26	27	28	24	25	26	28		7	24	25	28		24	28			
	7	21	23	24	29	7	24	26	34		7	24	29	31	32	7	24	26	29	31
	30	31	32	33							35	36				32	35			
	34	35																		
<i>Dynamic Destruction</i>																				
Laboratory	37	38	39	40	41	44	45	46								37	46			
Test stand	42	43	44	45	46	7	34	47	48		7	34	48	49		34	48	49	50	
	7	34	48	49	50	49	50													
Road	34	50	51			34	50				34	50				34	50	51		

The numbers give the literature references to the subject involved.

coefficient of friction on the speed, with occurrence of a maximum, similar to that mentioned by us³.

In the determination of the coefficient of friction a choice of compound formulation and type of rubber is possible. In this paper it is shown, however, that this does not suffice for a correlation with the gripping power. In addition to the coefficient of friction, the gripping ability of the tread pattern is an important factor. This is a function of the mobility, conformity to the supporting surface, and the effect of edges.

Measurements of tires made on test stands are a necessary supplement; for example, the procedure described by Bobeth⁶. Further measurement can also be made of the forces that can be transmitted in the direction of the periphery, that is, not merely measurements with pure rolling. For this, Williams and Clifton⁷ published a method by which it is possible to measure the braking force on an ice-coated test stand. Their paper calls attention to possible discrepancies caused by the curvature of the test drum when contrasted with the plane road surface.

The advantage of the test-stand measurements is that most of the scattering among the results of road tests can be avoided. In spite of this, road tests cannot be dispensed with. These include tests with towing devices, or experiments with suitably designed test cars or tests with ordinary vehicles, in which the measuring equipment can be installed for such tests, as described, for example, by Lessels⁸.

As dealt with by Williams and Clifton⁷, Grace and Winter⁹, and French and Gough¹⁰, the measurements comprised for the most part determinations of the coefficient of friction from braking tests and from the radial acceleration during travel on curves, the length of path on braking from a definite speed to a standstill, the maximum acceleration from rest, the maximum climbing ability, and the maximum attainable speed on ice. These measurements give the best information with respect to driving safety, for they involve not only the influence of the compound and the tread pattern, but also the type of vehicle and the nature of the road surface.

The importance of the latter influences is pointed out in the published works of Enders¹¹, von Bomhard¹² and Koessler¹³. The shock absorbers on the vehicle and the nature of the road determine the dynamic load on the wheels and, consequently, the gripping of the tires on the road. Special attention is devoted to carrying out the testing under conditions that correspond dynamically exactly to the actual service conditions.

EXAMPLES

Figure 1 gives an example of a laboratory measurement in which the coefficient of friction is represented as a function of the velocity. The measurements were made with a wet steel contact surface. Curve I is for a natural-rubber compound, curves II, III, and IV are for the same compound, but with increasing amounts of a wetting agent added to the distilled water. The interpretation of the effect of the wetting agent will not be gone into here, and the discussion will be confined to what is decisive for the question of the correlation.

The curves show an increase of the coefficient of friction, the occurrence of a maximum, and finally, depending on the type of compound, a decrease; in short, a strong dependence on the velocity. This proves that a single value for the coefficient of friction is not sufficient to evaluate a compound. If one wishes to judge compounds, or as here, the effect of wetting agents, the question

arises as to what velocity one should use for the comparison. The order would be different at lower velocities than at the maximum or at higher frictional velocities. If one does not know what velocities are decisive for service, then one cannot draw any conclusions from these measurements about the gripping power of the tire. From the increase of the coefficient of friction, one can deduce that not the rest friction but a certain relative motion must be presupposed, that is a certain slipping of tires in the peripheral direction⁸. The slip calculated for the maximum is, however, still much smaller than that which,

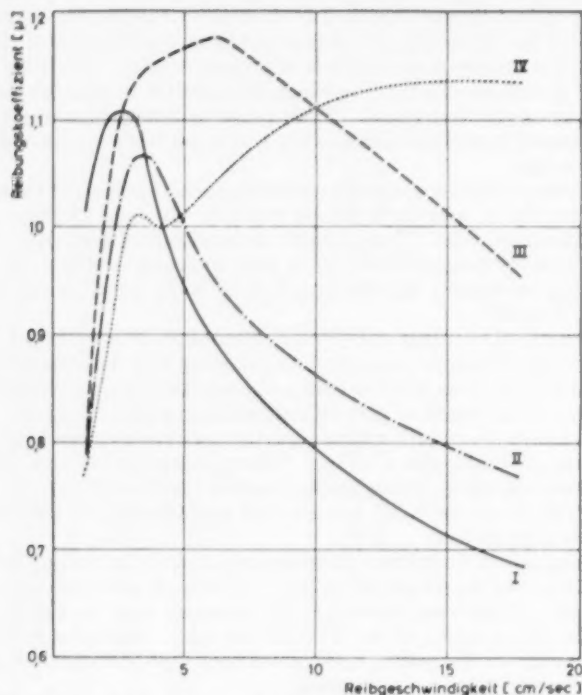


FIG. 1.—Coefficient of friction (wet) as a function of the contact velocity. Stationary layer: sand-blasted steel. Test-piece plain, not profiled. I. Normal tire compound (natural rubber) with distilled water. II. 0.002% wetting agent in the boundary layer. III. 0.1% wetting agent in the boundary layer. IV. 0.5% wetting agent (sodium naphthenate) in the boundary layer. Ordinate: Coefficient of friction. Abscissa: Contact velocity (cm./sec.)

on the average, occurs in the case of tires. From this it can be concluded that those values of velocity which are to the right of the maximum are more essential in the case of tires, and that the so-called gripping friction at rest does not necessarily make it possible to draw any general conclusions.

Table II gives the values of the coefficient of friction measured at 20 cm. per sec. frictional velocity for the same compound as that in Figure 1. For comparison, however, incisions were made in the rubbing surface of the test-piece, similar to the tread grooves on tires. The coefficient of friction is appreciably increased over that of the untreated sample, but to a lesser degree if the cuts are too narrow. This simple example shows that, besides the type of com-

pound which here remained the same, a suitable profiling, can impart, by the effect of mobility and of the edges, marked improvements, especially at high frictional velocities. From this it can be concluded that measurements in the laboratory are not sufficient to assess the holding ability of a tire.

This finding leads of necessity to expanded measurements on test stands, which give a better evaluation of the influence of the tread patterning. Test-stand measurements are made for the most part on drum test-stands. In this

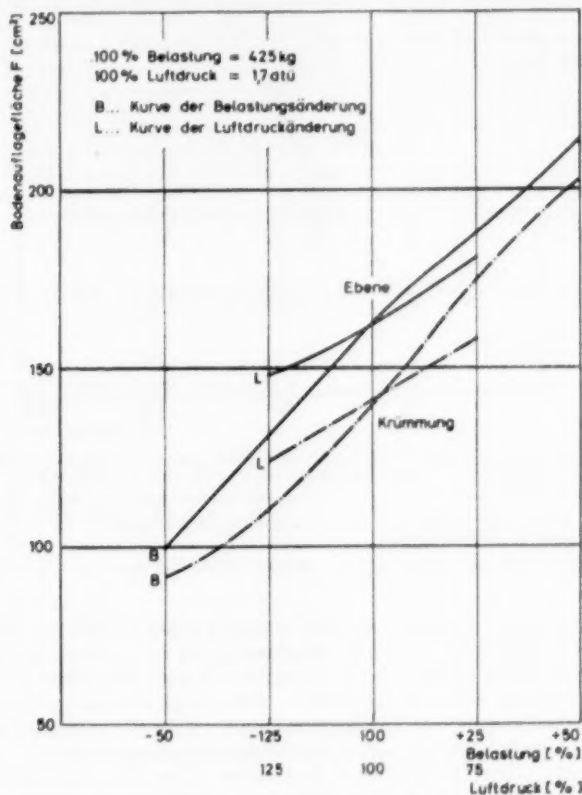


FIG. 2.—Area of contact of a smooth tire (6.40-13) as a function of load and air pressure for plane and for curved surface ($r = 80$ cm.) Ordinate: Contact area (cm.²). Abscissa: (upper scale) load (%); (lower scale) air pressure (%). (In figure 100% load = 425 kg, 100% air pressure = 1.7 atm.)

B....curve for load variation
L....curve for air pressure variation

connection it must be realized that because of the curvature of the drum there can occur deviations in the nature of the treatment compared with that on a plane surface. Figure 2 shows, for example, the contact areas of the plane surface and of the drum when the air pressure and the load are varied on a tire without tread profiles (6.40-13). With a change of about 25 per cent air pressure or load, a surface area is obtained equal to that in the case of the plane. This is for a drum diameter of 1.6 m. But it is not easy by means of this device

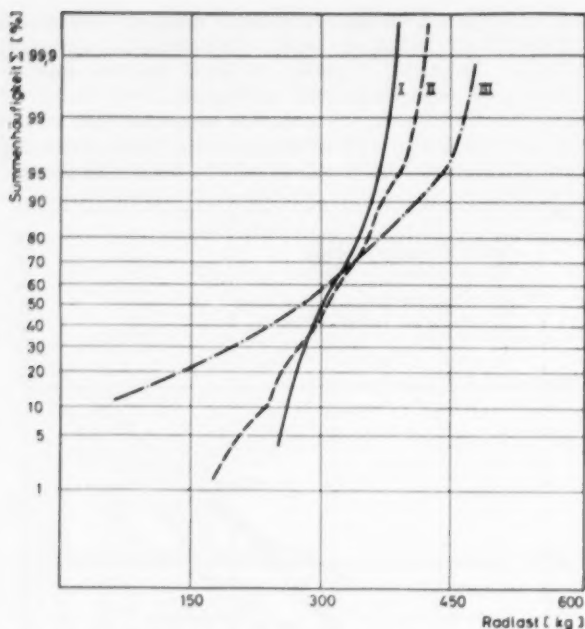


FIG. 3.—Summation frequency distribution of the ground pressure for different modes of driving and nature of road (according to measurements of von Bomhard).

Smooth asphalt, 51 km./hr.

Concrete road with frost cracks 85 km./hr.

I. With shock absorbers.

III. With shock absorbers

II. Without shock absorbers.

Ordinate: Summation frequency (%). Abscissa: Wheel load (kg.)

to adapt the pressure distribution and the spring arrangement, which are likewise decisive for gripping power, to the plane at the same time. In each individual case one must ask oneself the question, whether the difference from the case of the plane can be neglected or not. Only large drum diameters or turntable disks ("merry-go-round") offer a way out. The advantage of test-stand measurements is that a large part of the deviations among results of road tests are eliminated. Nevertheless, road tests cannot be dispensed with. Their importance and the understanding of the test conditions are illustrated in the following example.

TABLE II
FRICTION COEFFICIENT AGAINST SMOOTH STEEL AT 20 CM.
PER SECOND WHEN WET WITH DISTILLED WATER

Tread (Natural rubber)	Smooth	With parallel incisions at right angles to direction of motion Ratio of width to depth	
		2.5:1	1.2:1
Friction coefficient	0.53	1.0	0.8

It is well known that, in practical service, the load on the wheel does not correspond to the static load, but underloads and overloads occur. The underloads diminish the gripping power and the driving safety. Measurements of the dynamic wheel loads were made, for example, by von Bomhard¹², and these we have evaluated as follows.

The whole length of the recorder strip showing wheel load vs. time was divided into individual sections, i.e., time elements. The wheel loads corresponding to the sections were arranged in the order of their frequency and represented according to the cumulative probability. Figure 3 gives their distribution for a road with smooth asphalt with (I) and without (II) shock absorbers, and for a concrete surface road (Kleinpflasterstrasse) with numerous frost cracks and with shock absorbers (III). The flatter the course of the curves, the greater is the deviation of the wheel loads from the average value. It can be seen that the axle damping plays a decisive role in the distribution of the wheel loads. A greater damping gives better equalization of underloads and overloads. If the vehicles differ in their damping behavior, the same tires may be evaluated differently. Table III makes a still clearer evaluation.

TABLE III
EVALUATION OF THE DISTRIBUTION OF WHEEL LOAD ACCORDING
TO MEASUREMENTS BY BOMHARD¹²

During	10	20	30	40% of the travel time the wheel load is on:
Street with smooth asphalt (51 km. per hr.)				
(I) With shock absorbers	87	91	94	97% of the average wheel load
(II) Without shock absorbers	77	84	90	96% of the average wheel load
Concrete with frost cracks (85 km. per hr.)				
(III) with shock absorbers	16	51	73	88% of the average wheel load

At the higher speed of 85 km. per hour, for example, and with a bad road surface condition, the wheel, in spite of the damping, presses on the road with less than 51 per cent of the average load for 20 per cent of the travel distance, i.e., only one-fifth. The tires are floating during a considerable part of the travel. In these moments, smaller forces are able to cause skidding than would be the case in rolling along under constant load, and this lowers the driving safety. In this case the danger of skidding does not depend on the tire alone.

If one were to conduct static measurements or towing measurements at low speeds over the same roads, however, then one would not be aware of these dangers.

This example shows that conditions similar to actual service are necessary for the evaluation.

SUMMARY

Laboratory measurements of the coefficient of friction do not suffice for a complete correlation with respect to the driving safety of tires. The gripping power of a tire is not determined by the coefficient of friction of the compound alone, but also in large part by the tread pattern. This is indicated by both test-stand and road tests.

In test-stand experiments it must be realized that the pressure distribution and the contact areas are different with a drum from those with a plane surface, and that for this reason there will be discrepancies.

Only an evaluation by road tests with vehicles under conditions comparable with regular service, and with exact information regarding type of vehicle, type of spring equipment, and nature of the road, offer a complete picture of the complex characteristic of travel safety.

ABRASION

The wearing behavior of the tread is one of the characteristics of a tire which are of most interest to the user. Rubber suppliers, and producers of raw materials and of tires are constantly striving to improve all the properties that contribute to decreased wear.

DISCUSSION

The great importance of suitable abrasion test methods for compound development is evident from the great number of publications about testing equipment and methods, and it is to be assumed that a still greater number are in use. A compilation of the different methods has been given by Buist¹⁴.

In recent years great advances have been made in the understanding of abrasion processes¹⁵, among which we draw especial attention to the studies of Schallamach¹⁶. Equipment has been abandoned, redesigned, and rebuilt, and in individual series of experiments good correlation with road test results has been found¹⁷.

In this paper it is shown that, for such a correlation, the question of the intensity of the abrasion is one of great importance. This fact has been stressed by Buist¹⁵, Burns and Storey¹⁸, Adams and coworkers¹⁹, Howland and coworkers²¹, Biard and Svetlik²², and Newton and coworkers²³. We also called attention to an example which related to the comparison of different types of rubber³, whose classification depends to a marked degree on the intensity of the test. For these types of rubber, Fromandi and Oettner²⁴ obtained similar results from practical road tests.

It will be further shown in this paper that a better approximation of the laboratory testing to the nature of the abrasion process on the road, for example, with respect to the temperature in the friction surface and the way it is cleaned, will effect an improvement in the correlation.

It is necessary to take into account the intensity and the adaptation to the nature of the service action in order to improve the correlation, but this is not sufficient. Tire abrasion, as we have shown²⁵, can be thought of as the combined resultant of the inherent abrasion of the compound and of the work of abrasion. The abrasion energy is influenced by the tire structure, tread pattern, condition of the vehicle, travel conditions, and road characteristics.

The importance of the tread profile on the abrasion has been pointed out also by Holt and Cook²⁶ and by Roberts²⁷. In this paper it is shown that test-stand measurements can give information about the abrasion energy in the tread. Here the effectiveness of the shearing and circumferential forces and of the coefficient of friction in influencing the abrasion is stressed.

Test-stand measurements are also employed for the direct determination of abrasion. Braber²⁸ reports on preliminary work in this connection, and Astin²⁹ on types of test stand intended to give more rapid and more uniform results than road tests. Williams and Clifton⁷ describe abrasion experiments on drums

with lateral forces acting on the tire. It is pointed out in this paper⁷ that the one-sided wear which occurs makes periodic shifting of the tires necessary.

Road tests give the best correlation with service. Directions for carrying out such tests are given by Stiehler, Mandel, and coworkers³⁰, Stechert and Bolt³¹, Sjöthun and coworkers³², and the National Bureau of Standards³³. The influences of type of compound, mode of travel, wheel position, temperature, and climate are evaluated according to statistical points of view. Recent reports by Amon and Dannenberg³⁴ stress the necessity of taking into account the driving conditions and the intensity in road tests as well. Abrasion figures differing by more than one order of magnitude can be produced by the manner of driving, type of road, and the load³⁵. It is not sufficient to use a single value from one test to characterize abrasion behavior³⁶ and then generalize from this result.

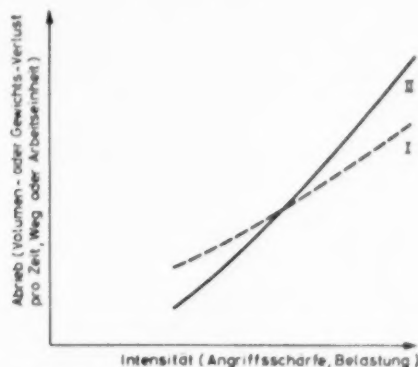


Fig. 4.—Abrasion as a function of the intensity (load, severity of attack) for two compound types I and II. Ordinate: Abrasion (volume or weight loss vs. time, distance, or unit of work). Abscissa: Intensity (load, severity of attack).

EXAMPLES

When the abrasion values are plotted against the intensity of the friction, curves like those in Figure 4 are obtained. This figure is purely schematic to show the type of behavior, so no scales are shown for the coordinates. For the following discussion it makes no difference whether we use weight or volume loss as a function of the same time, same distance, or same frictional work, or whether the intensity is varied by increasing the contact pressure or the roughness of the contact surface of the underlayer. (Temperature changes are not counted as intensity changes). In all cases there can occur intersections like that in Figure 4. At lower intensity, for example, compound II (synthetic rubber) is superior, while at higher intensity compound I (natural rubber) is superior. If it is desired to arrange the compounds in order of merit, the question again arises, just as in the case of the determination of the coefficients of friction, as to what test conditions one should select for such an ordering. It is easier to answer this question if one has a clear idea of the intensity that exists in practice.

For this purpose let us consider Table IV. Here the measure of the intensity is the loss of thickness in μ per minute. This somewhat unusual unit of measure need be of no concern, for we are here directing our attention only to the order of magnitude of the wear.

A normal driver travels, for example, 40,000 km. at an average speed of 65 km. per hour and wears off 10 mm. of the tread pattern. This corresponds to about 0.3μ per minute. This value is shown in the last column of the table. The other values show the intensities found in road tests on test stretches (Nuerburg circuit). In the latter the intensity is already greater by about one order of magnitude than in normal travel.

In the second part of Table IV are values obtained in similar manner from laboratory methods. In a test method with poor correlation, which is even partly negative, the intensity of abrasion is even greater. Compared to actual service, it is about three orders of magnitude greater.

In a method with good correlation, which we have already described³, the intensity is only one or two orders of magnitude higher. If one makes the comparison with severe driving conditions on the test track, then it is of the same

TABLE IV
COMPARISON OF THE ABRASION INTENSITY IN MU PER MINUTE
FOR DIFFERENT TRAVEL AND TEST CONDITIONS

Type	Average velocity (km./hr.)	Intensity (μ /min.)
Road Tests (May-Oct.)		
(a) Normal travel	65	0.27
(b) Road test travel		
Truck (8.25-20)	50	0.6
Truck (8.25-20)	63	0.63
Private car (6.40-13)	83	0.95
(c) Test route (Nuerburg circuit)		
Truck (8.25-20)	62	7.6
Private car (6.40-13)	86	9.5
Laboratory Tests		
(a) Methods with poor correlation (DVM-DIN 53516): $r = 0$		240
(b) Methods with good correlation ³ : $r = 0.8$		20
(c) Lambourn method with good correlation ²⁰		26

order of magnitude. In the third method mentioned, good correlation is also reported, and, according to data in the literature, the intensity is about the same as that in the second method²⁰. From these figures one can conclude that the intensity in testing must not depart from that of actual service by too many orders of magnitude.

In addition, one must take into consideration the nature of the treatment. Factors in this are the friction temperature and the cleaning of the friction zone. The major part of the frictional work is converted into heat in the boundary layer. In a tire, every profile element is exposed by the rolling motion to only a brief moment of friction, i.e., only while it is passing through the contact surface. Between exposures the profile element can cool off. This effect is also promoted by the cooling action of the new road surface regions that the element comes into contact with. In most abrasion testing equipment in the laboratory, one and the same place is in contact with the friction surface of the machine during the whole test period, or has only brief negligible cooling

periods. Provisions for cooling and good heat conduction in the friction surface contribute to the improvement of the test conditions.

The friction temperature also affects the so-called lubricating film formation. In Figure 5 the surfaces of a test-piece are shown after different times of exposure to friction. Arrow B shows the direction of motion of the friction underlayer, L the direction of illumination, E the zone of entrance, A the exit zone of the friction underlayer. These indications suffice to enable one to get a sort of plastic impression from the pictures. It can be seen that after only a few seconds of friction a sort of tarry lubricating film has formed on the surface of the test sample. This is inevitably connected with the abrasion process, that

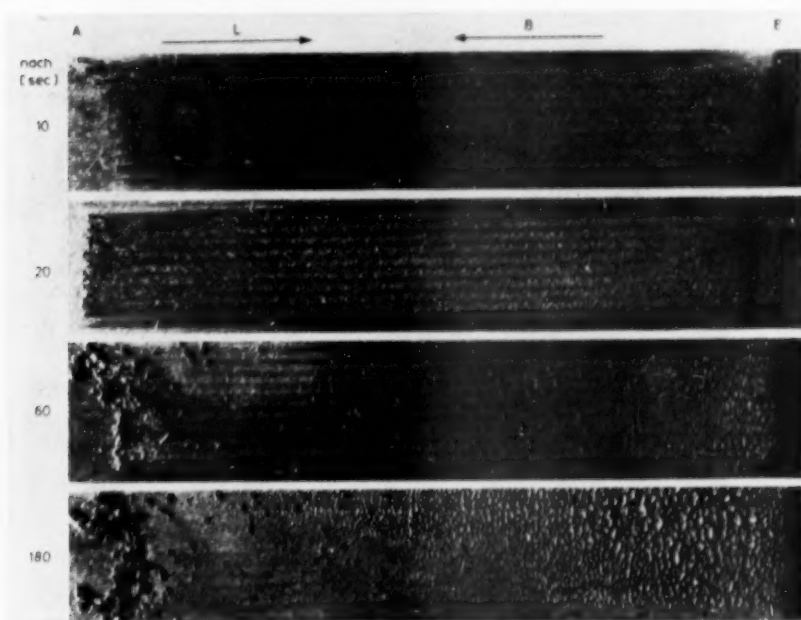


FIG. 5.—Worn surfaces after various wear times. L = Direction of illumination. B = Direction of motion. E = Initial zone of friction surface. A = Final zone of friction surface. Ordinate: After-seconds.

is, it is an integral part of it. If this takes place to a marked degree in laboratory testing, the film acts as a protective layer, through which the friction underlayer can penetrate only by a sort of raking action, and which tends to protect the test piece from further abrasion. Thus the abrasion results are falsified.

If steps are taken to remove or to prevent formation of this protective film, the test method is improved. Extraction of the test-sample before the test in order to remove softeners which tend to favor the formation of the lubricating film, although disadvantageous in some ways, or cooling during the test, lessens this falsification by the film. Another way of removing the lubricating film can be seen from Figure 5. The abrasion pictures result from a procedure reported by us³, according to the principle of rope friction. In this there is a

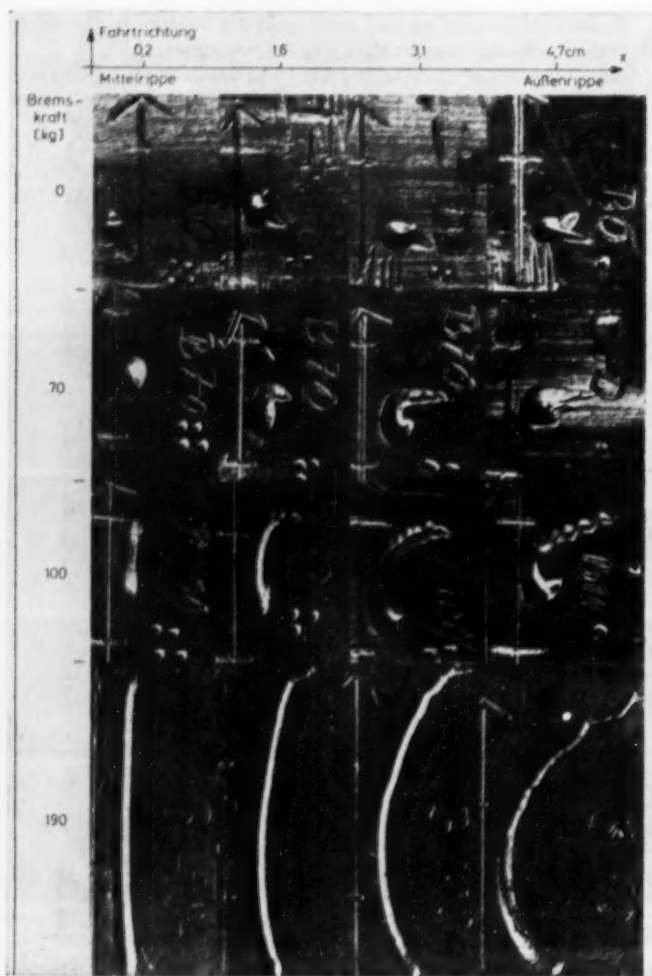


FIG. 6.—Pressure-path-impressions on 6.40-13 tires at high friction coefficient. Ordinate: Braking force (kg.). Abscissa: Vertical arrow: travel direction, horizontal arrow: middle rib, outer rib (x).

uniform pressure gradient from the entrance point to the exit point. This can also be seen from the degree of wear. The pressure is greatest in the entrance zone and practically zero in the exit zone. The film and the abraded rubber particles tend, consequently, to roll up into cylindrical crumbs and to move away from the friction zone in the direction of the pressure drop. They accumulate outside of the exit zone, and the friction zone is automatically cleaned.

The measurements with laboratory equipment can show good correlation with that part of the wear that is a function of the type of compound after these measures are taken. However, the type of tread pattern and the tire structure, the type of vehicle, and the manner of driving, as well as the kind of road and

the climate, contribute a further portion of the wear. As a first approximation this part can comprise the frictional work which we have already discussed earlier²⁵. This proves that the same compound shows different degrees of wear with different amounts of frictional work.

To get an idea of this frictional work, let us consider Figures 6-8. These show the "pressure-path-impressions". Without going into more detail concerning the rather difficult evaluation, we shall only state here that, for these measurements, small steel particles are built into the tire surfaces. These follow the movements of the tread elements and make impressions or scratches on a metal plate when the tire is rolled over it. Their width is a measure of the

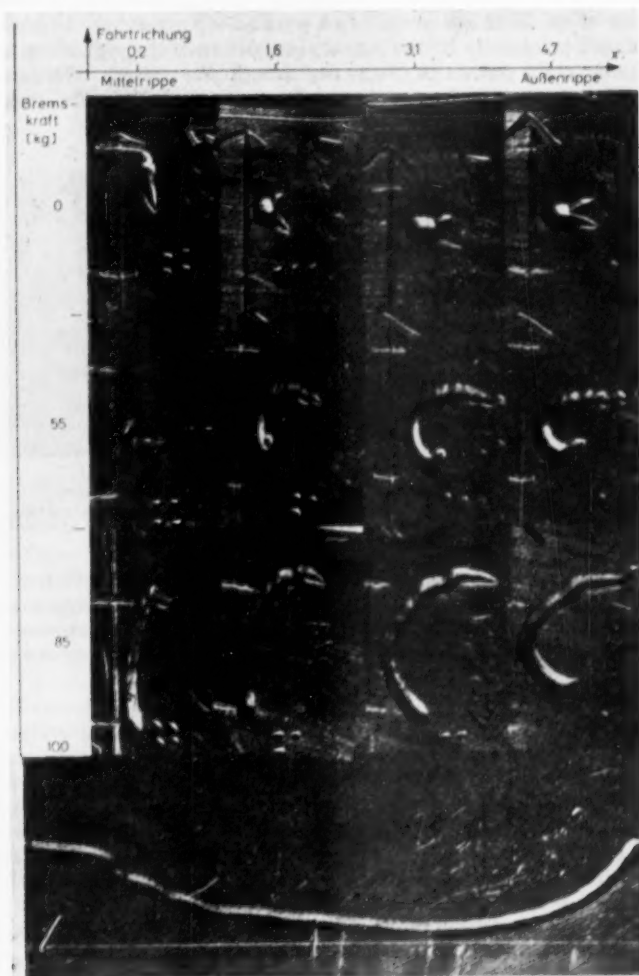


FIG. 7.—Pressure-path-impressions on 6.40-13 tires at low friction coefficient. Ordinate: Braking force (kg.). Abscissa: Vertical arrow: travel direction, horizontal arrow: middle rib, outer rib (x).

pressure, their length shows the path, and the product multiplied by the coefficient of friction corresponds to the frictional work.

In Figure 6, the pressure-path-impressions are shown for a 6.40-13 tire with different circumferential forces for the middle rib, at the left of the picture, for the intermediate ribs and the outer rib at the right of the picture under magnification. The circumferential forces in this case are braking forces. On the other half of the tire, which is not shown, the pressure-path-impressions are approximately the mirror image of those shown. The arrows in the photomicrograph show the direction of travel. The somewhat disturbing symbols served to denote the experiment on the metal plates and the films. Even qualitative consideration shows the influence of a circumferential force on the magnitude of the frictional work. In a pure rolling action, the frictional work is determined principally by the lateral constriction of the profile and is, therefore, greater in the outer ribs of the tire than in the center. With increasing circumferential force the frictional work increases; in fact, in the inner ribs as well.

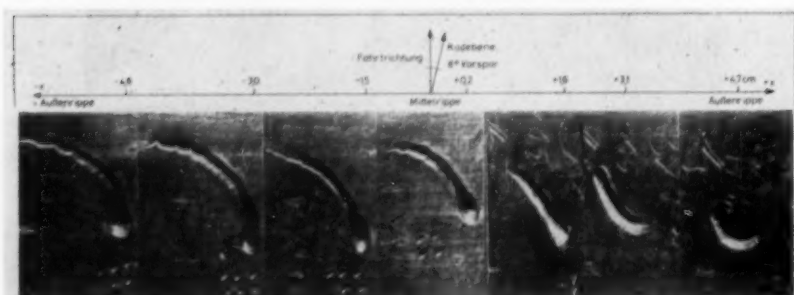


Fig. 8.—Pressure-path-impressions on 6.40-13 tires having 7 ribs at 115 kg. braking force and 8° angle between wheel plane and direction of travel, with high friction coefficient. Load 425 kg.; tire inflation pressure 1.7 atm. Ordinate: Vertical arrows: Travel direction, plane of wheel, 8°, wheel plane angle to travel direction. Horizontal arrow: outer rib, $-x$; outer rib, $+x$. Mittlere Rippe is the middle rib.

Figure 7 shows similar conditions but at a lower friction coefficient. Even at much smaller circumferential forces there is a noticeable sliding or slipping. At 100 kg. circumferential force, there is only a pressure-path-impression from the outer rib horizontally, since otherwise with the same scale there would not have been enough room to show the results.

Comparison of both figures illustrates also the influence of the coefficient of friction on the abrasion. With a low coefficient, the circumferential forces increase the friction path. The increase of path length at too low a coefficient can be greater on a percentage basis than the decrease of the coefficient itself, that is, the resulting frictional work is greater. With a high coefficient, on the other hand, greater circumferential forces can still act essentially without appreciable friction path, so that the frictional work is slight. If, however, the path of the contact surface of the tire is a forced one (see also Figure 8) then, with high coefficient, the frictional work is greater than it is with a small one.

From this we can deduce the following. Even in road tests it is necessary to take the travel conditions and the slip into consideration for a more precise definition of the frictional work. In a road test there is no advantage in attempting to measure two or three compounds or tread patterns simultaneously

in one tire. This does, to be sure, reduce the dispersion of the test results, but there can also be a mutual effect of the tire segments which falsifies the result.

Figure 8 gives the pressure-path-impressions for the same tire with braking and an oblique position, that is, with the plane of the tire at an angle to the direction of travel. This latter is a well known procedure for the direct determination of the abrasion on drum type test stands⁷. In this case the pressure and the path direction are no longer symmetrically distributed with respect to the center of the tire. For this reason the microphotographs show all the ribs instead of only one-half of the tire. The wear picture of such a tire shows one-sided distortion. This type of abrasion test on test stands under these conditions does not make it possible to draw conclusions directly about the effect of the tread profile on the abrasion on a plane. However, as in the case of laboratory tests, it is possible to make judgments with respect to different compounds, provided one succeeds in eliminating the disturbing influences of temperature and lubricating films.

DISCUSSION

An improvement in the correlation between the portion of the wear that is determined by the type of compound is possible by adapting the abrasion intensity and the nature of the treatment to the service conditions. However, this part of the wear is not the whole action. A second component that is decisive is the frictional work. This is influenced by the coefficient of friction, the tread pattern and the tire structure, the type of vehicle, the manner of driving, and the nature of the road.

Test-stand measurements can give information about the importance of the frictional work. Direct abrasion determinations on test stands require that measures be taken to eliminate the partly distorted picture due to one-sided wear.

In road tests too, attention must be paid to the frictional work or the intensity of the treatment, since travel conditions and slipping also play a role in the abrasion measurement.

DYNAMIC DESTRUCTION

With the trend to higher travel speeds, heavier spring equipment, and high abrasion compounds, the question of crack formation and, to some extent also, of heat destruction by higher operating temperatures becomes more important.

A SURVEY OF THE PROBLEM

Buist and Williams³⁷ distinguish three groups of laboratory tests of dynamic destruction: destruction by pure internal heating, crack formation in the surface of the test sample, and combinations of both types.

The pure heat destruction is determined with the aid of the familiar flexometer, which operates with predetermined forced vibrations. Damping losses and heat conduction³⁸ determine the life before destruction occurs. Measurements of pure hysteresis with free or forced vibrations also belong in this group. They do not include the effect of heat conduction, which is of decisive importance for the operating temperature in tires. Comparative reviews of the various types of laboratory apparatus have been given by Kainradl and Haendler³⁹, Dillon and Gehman³⁹, and recently by Ball and Randall⁴⁰. The test fre-

quencies employed have been surveyed by Angioletti⁴¹. These are decisive with respect to the magnitude of the losses. Besides heat build-up, mechanical stresses also produce cracks directly, as reported by Gough and Parkinson⁴². Buist⁴³, and Williams⁴⁴ in particular have carried out studies with the De Mattia machine, as the best known method of the second group for testing crack formation without appreciable superimposed heat development, and also with the chain bending machine. In the third group is the rotary flexing machine⁴⁵ in which crack formation in the surface of a sample is influenced by the heat build-up in the interior.

The tests of all three groups show clearly that the nature and intensity are decisive for the correct ordering of test compounds.

In heat build-up, the order of the results depends decisively on whether the treatment involves constant deformation, energy, or force⁴⁶, or on what intensity of treatment and what temperature are chosen. Only with knowledge of the practical conditions is it possible to choose the proper type of test.

In crack formation, the tension on the elongation in the surface, i.e., the intensity, is decisive for the moment at which the crack starts to form or for the rate of crack growth, and for the relative rating of compounds. On the one hand, with increasing testing velocity, the results show smaller deviations⁴⁴. This is achieved by choice of sample shape⁴⁴ or by concentrating the load in single zones⁴⁵. On the other hand, with too great departure of the intensity from the conditions in service, differences in the ranking of the compounds appear, as we show in this paper.

An example that illustrates more precisely the complex nature of the treatment causing crack formation is shown in the work of Gehman and Clifford⁴⁷, in which a periodic stress acts on the test-piece in two perpendicular directions. In this work, a dependence of crack formation on the structure direction is established, to which we referred earlier⁴⁸.

In test-stand measurements, not only is there the effect of the compound, but also that of the tread profile and the tire construction. For judging crack formation, it is possible to build tires of segments of different compounds⁷, and in this way to reduce the deviations of the measured results. For crack growth too, methods have been published, e.g., by the National Bureau of Standards⁴⁹, in which cuts are made in the bottom of the grooves before the test and their development is measured after different times.

The resistance to rolling of a tire as a measure of internal losses is determined either by measuring the turning moment about the axis or with a pendulum motor, or by comparing the difference of power consumption between rolling of the tire, with and without load, as a function of the velocity⁷. With increasing curvature of the test drum and increasing velocity, with resulting standing waves along the circumference, as reported by Gardner and Worswick⁴⁷, higher rolling resistance and more intense heating than on the road are encountered. The effects are exaggerated over those in road tests. Large radii and air cooling are measures which tend to improve the tests. Zoeppritz⁴⁸ made measurements on test stands with a plane track and found that the results agreed with exhaustive road tests. Weber⁴⁹ has given comprehensive comparative figures on the influence of different driving conditions, such as air pressure, load, and speed, and has also pointed out the importance of simulating on the test stand the wind resistance corresponding to the velocity.

Recently Rinne, Sjothun, and Greer⁵⁰ have reported on some test conditions used in the methods for rolling resistance, for temperature measurements

on the test stand, and in road tests. Tires are tested not only with pure rolling but, to simulate service conditions, tires are driven in contact with a braked drum. After a running-in period, temperature measurements are made in the surroundings, in the air chamber of the tire, and in the boundary layer between tread and carcass. With regard to the correlation, these authors report that there is fundamental agreement between laboratory measurements of temperature and those on the test stand.

Thermal behavior is not sufficient, however, for evaluating dynamic destruction in service. In addition, breakdown or failure by ply or tread separation is one of those properties which cannot be foreseen by hysteresis measurements alone, and require special adhesion or bonding tests⁴⁰.

Among practical road tests, the work of de Decker⁴¹ should also be mentioned. He has reported on the relationship between hysteresis losses and fuel consumption.

EXAMPLES

In this section the examples relate only to dynamic crack formation. The relationships are similar for heat destruction. Figure 9 shows crack formation as a function of the intensity. Like Figure 4, this too is shown only schematically and is intended merely to illustrate what is stated below. Crack formation is measured as crack area⁴² or crack length, and is expressed in relative terms, i.e., in comparison with compound I. The figures were obtained with a machine designed on the De Mattia principle. Here the intensity can be varied readily by adjusting the stroke for equal elongation. In this way the flex angle is varied, and this is used as a measure of the intensity. It would be equally correct to use a different machine or to represent crack formation as a function of the elongation. In defining the flex angle, it should be understood that this means the angle between the two tangents to the outer surfaces of the test-specimens. In the completely flexed state it is zero degrees.

From this representation it is seen that, at high intensity, compound I shows up appreciably better, i.e., shows much less crack formation after the same running time, whereas compound II is superior at lower intensity.

Here we encounter the same fact as that found in assessing coefficients of friction (Figure 1) or abrasion (Figure 4). The question arises, at what intensity the ranking of compounds should be made. It is not enough to make a test at a single arbitrarily selected intensity, for one must have some knowledge of the service conditions in order to be able to simulate these, i.e., one must know the magnitude of the stresses and strains.

Without going into details concerning the various procedures, which we have already discussed in part⁴³, we shall give a few results of measurements of the magnitude of the stresses or the elongation in the test sample grooves of the tread profile. The magnitude and the course of the elongations in the surface layer depend on the shape of the grooves, as Figure 10 shows. Here the elongation is shown at complete flexing (angle zero degrees), for a parabolic (I) and a semicircular (II) groove, (corresponding approximately to the De Mattia form), as a function of position in the bottom of the groove. The figures denote microscopic scale divisions. The elongation in the middle of the parabolic groove (I) is about double the size of the other. From this it can be concluded that not only the compound but also the construction of a tire and its tread pattern design influence the crack formation.

In Figure 11 this maximum elongation is made equal to 1, and the relative elongation is shown as a function of the flex angle. At higher flex angles, the

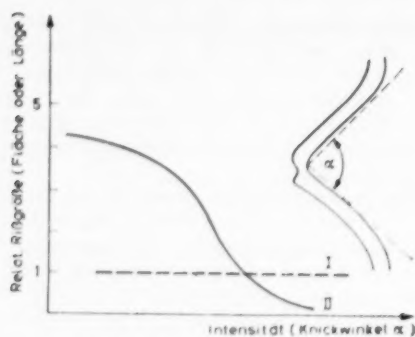


Fig. 9.—Crack formation as a function of the intensity (flex angle α) with compounds I and II. Ordinate: Relative crack size (area or length). Abcissa: intensity (flex angle α).

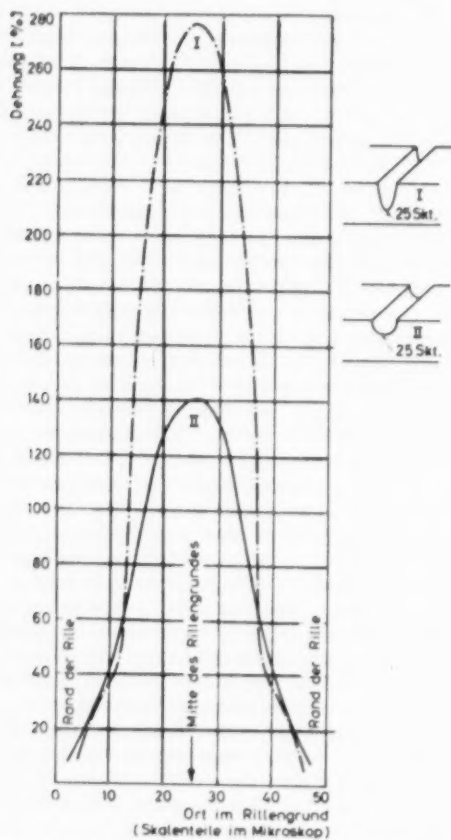


Fig. 10.—Surface elongation for different groove shapes (I and II). Ordinate: Elongation (%). Abcissa: Position at bottom of groove (scale divisions in microscope). (Vertical legends, left to right) border of groove, middle of groove bottom, border of groove. (Side figures I and II) 25 scale divisions.

running time for producing measurable cracks increases. The approximate test cycles corresponding to the flexing angles are shown. The order of magnitude of the extensions in laboratory, test stand, and road tests are included in the figure.

Here again can be recognized the philosophy which constitutes the leading idea of this paper: the closer the intensity of the test approximates the conditions of service, the better the correlation. The test must not be too severe. On the other hand, a severe test has the advantage of shorter duration and less deviation of the results. According to the aim of the test one or the other method is preferable. For routine control tests of technical compounds, whose uniformity it is desired to determine, the severe test will be employed⁴⁵. Compounds that are formulated very differently and whose practical ranking is not yet known should be tested at intensities as close as possible to those of actual service.

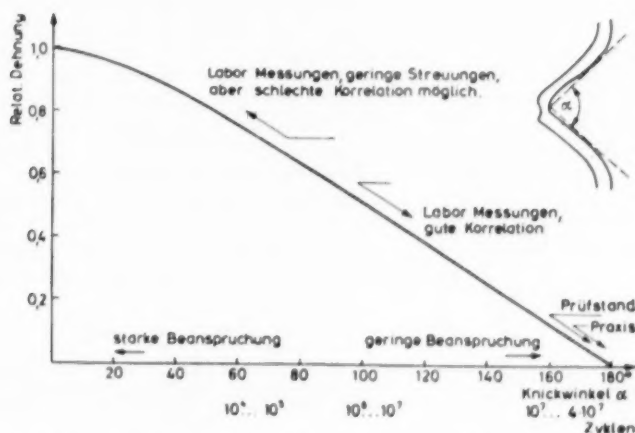


FIG. 11.—Relative elongation (based on maximum elongation = 1.0 for $\alpha = 0$) as a function of the flex angle. Relation between running time and severity of action on tires at groove bottom. Ordinate: Relative elongation. Abscissa: Flex angle α (upper scale). Cycles (lower scale). (Legends in figure reading down and left to right): Laboratory measurements, slight dispersion, but poor correlation possible. Laboratory measurements, good correlation. Severe action, weak action. Test stand Service.

Finally let us call attention to the comparison between a plane and a drum, a matter which is, in fact, of decisive importance for determining the dynamic behavior, for example, rolling resistance and heat destruction on test stands. In Figure 12 the elongations in the ground contact region and in the diametrically opposite region in the innermost part of the carcass are shown for a 6.40-13 tire. These elongations are imparted to the compound in the side wall and tread. The greater severity in the curved surface over that of the plane can be seen, especially in the ground contact region of the side wall. The effects are exaggerated compared with those in road tests. This fact must be borne in mind if conclusions are to be drawn from measurements carried out on test stands.

DISCUSSION

In the determination of destruction by heat alone, of mechanical crack formation, and of combinations of these two effects, it is important to consider the nature and intensity of the treatment in laboratory measurements. Corre-

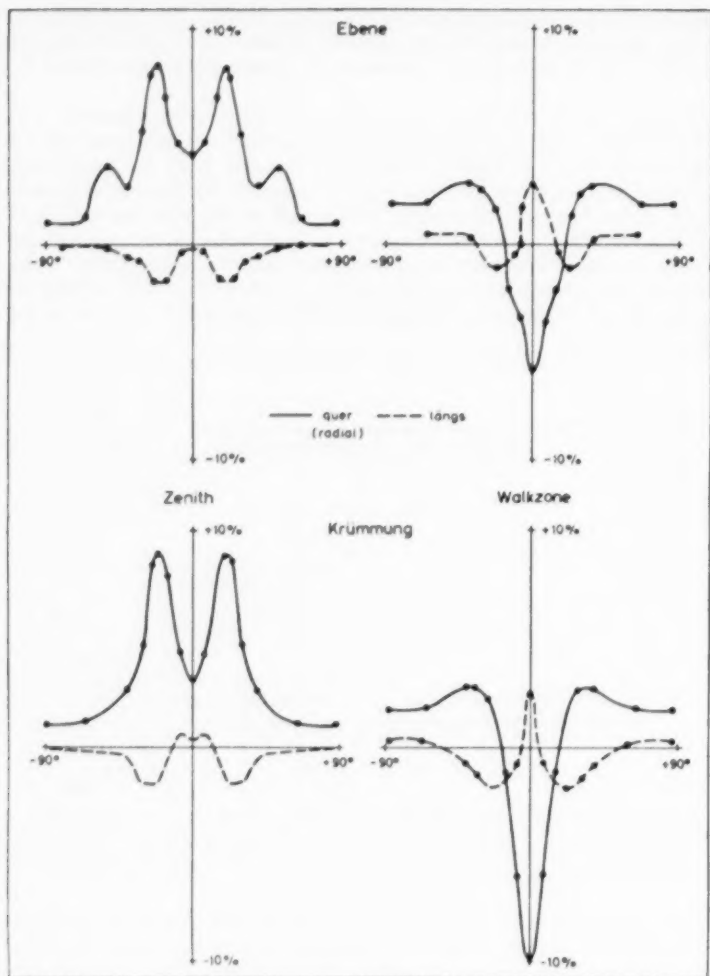


Fig. 12.—Percentage elongation in the tire inner wall (6.40-13), in ground contact region and diametrically opposite region, longitudinal and transverse. Comparison between plane and curved surfaces ($r = 80$ cm.). (Legends in figure).

Plane
 — transverse (radial) — longitudinal
 Curved Surface

lation with the crack formation which occurs in service is obtained if the tests are made at low intensity. In this case, long testing periods and greater variations in the results are unavoidable. Only for control tests of the uniformity of known compounds are severe, rapid, more precise test methods suitable.

In test-stand measurements, besides the effect of the compound, the tread pattern and the tire construction also play a decisive role with respect to heat

build-up and crack formation. Here the discrepancies between the severity of the action on a drum, compared with that on a plane, manifest themselves.

For dynamic destruction, there is a correlation of laboratory and test-stand evaluation with road tests and normal service. The first two test methods are thus the most significant with respect to this property.

CONCLUDING REMARKS

The only way to get a complete picture of the characteristics of tire treads is to classify the tests according to the influence of the compound, construction, type of vehicle, and type of road. Only by adapting tests in the laboratory, on the test stand, and on the road to the nature and intensity of practical service conditions, can good correlation be expected.

Laboratory tests show at most the effect of the compound and possibly that of the nature of the road (roughness) and that of the climate (temperature). It is reserved for test stand and road experiments to bring out those properties that are affected by the tread pattern and the type of vehicle.

We see as an essential task of laboratory testing technique not so much the creation of new complicated laboratory testing apparatus, as in better and better analysis, using new measuring methods, of the action on tires on test stands and in service, in order from this to find improvements in the available test apparatus and to base these on definite unfalsified elementary processes. The knowledge of the practical conditions not only has the advantage of improving the correlation, but makes it possible even in advance to strive for a goal-seeking development aimed at bettering the tire characteristics, since then one knows in advance what conditions are involved.

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REFERENCES

- ¹ Conant, Dum, and Cox, *Ind. Eng. Chem.* **41**, 120 (1949).
- ² Boonatra, *Trans. Inst. Rubber Ind.* **26**, 281 (1950).
- ³ Kern, *Kautschuk u. Gummi* **5**, WT 88 (1952).
- ⁴ Weinbrenner and Ecker, *Kautschuk u. Gummi* **6**, WT 42 (1953).
- ⁵ Wilkinson, *India Rubber World*, **128**, 475 (1953).
- ⁶ Bobeth, *Rev. gén. caoutchouc* **31**, 804 (1954).
- ⁷ Williams and Clifton, *Proc. Third Rubber Technol. Conf. London*, 1954, p. 512.
- ⁸ Lessels, *Mach. Eng.*, **61**, 125 (1939).
- ⁹ Grace and Winter, *India Rubber World* **126**, 633 (1952).
- ¹⁰ French and Gough, *Intern. Auto. Congress*, Sept. 1954, published in *Automobiltech.-Z.*
- ¹¹ Endere, *Automobiltech.-Z.* **56**, 249 (1954).
- ¹² Von Bonhard, *Automobiltech.-Z.* **56**, 300 (1954).
- ¹³ Koesler, *Automobiltech.-Z.* **56**, 305 (1954).
- ¹⁴ Buist, *RUBBER CHEM. & TECHNOL.* **24**, 483 (1950).
- ¹⁵ Intern. Symposium on Abrasion and Wear, Nov. 14-17, 1951, in Delft.
- ¹⁶ Schallamach, *Trans. Inst. Rubber Ind.* **28**, 256 (1952); *RUBBER CHEM. & TECHNOL.* **26**, 230 (1953).
- ¹⁷ Kern, *Kautschuk u. Gummi* **5**, WT 88 (1952); Burns and Storey, *Ind. Eng. Chem.* **44**, 825 (1952); *RUBBER CHEM. & TECHNOL.* **26**, 188 (1953); Adams, Reynolds, Messer, and Howland, *RUBBER CHEM. & TECHNOL.* **25**, 191 (1952); Howland, White, and Messer, *RUBBER CHEM. & TECHNOL.* **27**, 977 (1954).
- ¹⁸ Buist, *India Rubber J.* **121**, 180 (1951); *RUBBER CHEM. & TECHNOL.* **25**, 107 (1952).
- ¹⁹ Burns and Storey, *Ind. Eng. Chem.* **44**, 825 (1952); *RUBBER CHEM. & TECHNOL.* **26**, 188 (1953).
- ²⁰ Adams, Reynolds, Messer, and Howland, *RUBBER CHEM. & TECHNOL.* **25**, 191 (1952).
- ²¹ Howland, White, and Messer, *RUBBER CHEM. & TECHNOL.* **27**, 977 (1954).
- ²² Biard and Svetlik, *India Rubber World*, **127**, 363 (1952); *RUBBER CHEM. & TECHNOL.* **26**, 731 (1953).
- ²³ Newton, Scott, and Willott, *J. Rubber Research* **17**, 75 (1948).
- ²⁴ Fromandi and Oettner, *Kautschuk u. Gummi* **7**, WT 212 (1954).
- ²⁵ Kern, *Kautschuk u. Gummi* **6**, WT 42 (1953).
- ²⁶ Holt and Cook, *Natl. Bur. Standards J. Research*, Research Paper No. 2.
- ²⁷ Roberts, *S. A. E. Journal* **44**, 243 (1939).
- ²⁸ Braber, *Proc. Intern. Symposium Abrasion and Wear*, Rubber-Stichting, 1951, p. 57.

- ¹⁹ Astin, *India Rubber World* **128**, 365 (1953).
- ²⁰ Stiehler, Neel, and Mandel, *Trans. Inst. Rubber Ind.* **27**, 298 (1951); Mandel, Steel, and Stiehler, *Ind. Eng. Chem.* **43**, 2901 (1951). Stiehler, Rickey, and Mandel, *Rubber Age* **73**, 201 (1953).
- ²¹ Stechert and Bolt, *Anal. Chem.* **23**, 1641 (1951); *RUBBER CHEM. & TECHNOL.* **25**, 321 (1952).
- ²² Sjöthun, Greer, and Rhodes, *Rubber Age* **74**, 231 (1953).
- ²³ Anonymous, *Rubber Age* **71**, 361 (1952).
- ²⁴ Amon and Dannenberg, *India Rubber World* **131**, 770 (1955).
- ²⁵ Astin, *India Rubber World* **128**, 365 (1953); Schidrowitz, *Goodyear News*, Spring 1950; *India-Rubber J.* **119**, 60 (1950).
- ²⁶ Biard and Svetlik, *India Rubber World* **127**, 363 (1952); *RUBBER CHEM. & TECHNOL.* **26**, 731 (1953); Amon and Dannenberg, *India Rubber World* **131**, 770 (1955).
- ²⁷ Buist and Williams, *India Rubber World* **124**, 320 (1951).
- ²⁸ Kainradi and Haendler, *Kautschuk u. Gummi* **7**, WT 1, 34 (1954).
- ²⁹ Dillon and Gehman, *India Rubber World* **115**, 61, 217 (1946).
- ³⁰ Ball and Randall, *India Rubber World* **131**, 795 (1954).
- ³¹ Angioletti, *Kautschuk u. Gummi* **8**, WT 219 (1955).
- ³² Gough and Parkinson, *India-Rubber J.* **20**, 219 (1942).
- ³³ Buist, *Trans. Inst. Rubber Ind.* **29**, 72 (1953).
- ³⁴ Buist and Williams, *Trans. Inst. Rubber Ind.* **27**, 209 (1951).
- ³⁵ Kern, *Kautschuk u. Gummi* **8**, WT 195, (1955).
- ³⁶ Gehman and Clifford, *India Rubber World* **131**, 365 (1954).
- ³⁷ Gardner and Warwick, *Trans. Inst. Rubber Ind.* **27**, 127 (1951).
- ³⁸ Zoepfritz, *Automobiltech.-Z.* **44**, No. 13 (1942).
- ³⁹ Weber, *Automobiltech.-Z.* **56**, 325 (1954).
- ⁴⁰ Rinne, Sjöthun, and Greer, *Rubber Age* **76**, 709 (1955).
- ⁴¹ De Decker, Houwink, and van Amerongen, *Proc. Third Rubber Technol. Conf. London*, 1954, p. 749.

THE INFLUENCE OF THE HARDNESS OF RUBBER ON ITS COEFFICIENT OF STATIC FRICTION WITHOUT LUBRICATION *

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In the friction of rubber on other solid materials, the coefficient of friction μ depends¹ on the load N , according to the equation:

$$\mu = \mu_{\infty} + \frac{F_0}{N} \quad (1)$$

where μ_{∞} is the minimum value, determining the value of μ under large loads (where $F_0 \ll N$); and F_0 is the tangential component of the forces of molecular attraction between the materials, determining the value of μ under small loads, where μ_{∞} is a comparatively small value².

This equation is based on Deryagin's theory of a binomial law of friction for solid materials. In connection with this, it was shown experimentally that, in the friction of crossed filaments³, the load has exactly the same kind of effect on the value of this friction as it has on the friction of high polymers and other solid materials.

Thus, with ordinary samples, also, we find¹ that the load exerts the same sort of influence on the friction of rubber articles as on that of other solid materials. But as for the exact form of the equation, this need not be exactly the same for the friction of other solid materials as for rubber, in as much as the latter is deformed to a far greater extent as a result of the load, and this cannot fail to cause a difference in the hardness of the rubber itself. Actually, according to this equation, F_0 is the tangent of the angle of slope of the straight line of μ plotted against $1/N$, where F_0 is constant. However, in Figure 1a, for soft rubber stocks, a considerable deviation from linearity can be observed⁴.

In the present work, an attempt was made to render Equation (1) more precise by taking into account two experimental facts which are evident in this figure: that the angle of slope (i.e., F_0) decreases with an increase of $1/N$ (i.e., with a decrease of the load); and that the lower the hardness of the rubber, the greater is this effect.

Both phenomena can be understood in the light of Deryagin's theory⁵, according to which F_0 is proportional to the actual area of contact; this was verified experimentally by a study of the friction of various materials⁶. On the basis of this theory, an attempt was made to relate F_0 to the pressure P of the load and to the hardness of the rubber.

Let us designate the hardness of the rubber by the conditional quantity h , which ranges within limits of 0 and 1. Then F_0 may be described by the equation:

$$F_0 = A \cdot S \cdot P^{1-h} \quad (2)$$

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by Malcolm Anderson from the *Doklady Akademii Nauk S.S.S.R.*, Vol. 99, No. 3, pages 431-434 (1954).

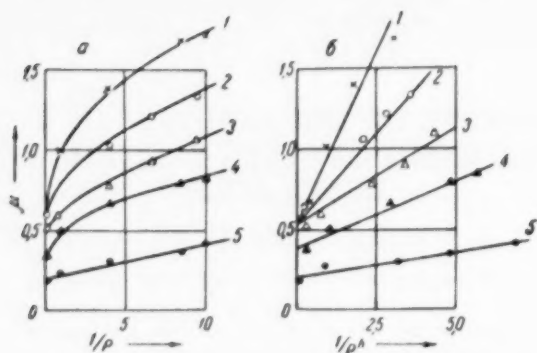


Fig. 1.—The relation between the coefficient of friction μ and pressure P of the load (in kg. per sq. cm.) in the friction on steel of a rubber stock based on the polymer SKN-26, with various loadings of graphite. 1. $C = 10$, $h = 0.45$. 2. $C = 45$, $h = 0.65$. 3. $C = 60$, $h = 0.68$. 4. $C = 80$, $h = 0.73$. 5. $C = 120$, $h = 0.83$. (C = parts of graphite per 100 parts of the polymer; h = hardness of the rubber.) The abscissa of Figure 1a represents the quantity $1/P$; that of Fig. 1b, $1/P^2$. The ordinate on both represents the coefficient of friction μ .

since the area of actual contact is proportional to the area of the nominal surface of friction S . This equation expresses qualitatively both of the facts noted above (the positive effect of the load and the negative effect of the hardness) and is accurate for the extreme values of h . That is, if the material is plastic ($h = 0$), the area of contact is proportional to the load ($F_0 = AN$), which reduces Equation (1) to Amontons' law⁵ ($\mu = \text{constant}$). On the other hand, if the material is absolutely hard ($h = 1$), then the area of contact is not affected

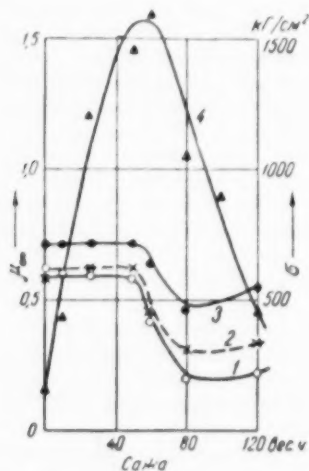


Fig. 2.—Comparison between the influence which the quantity of carbon black (in a stock based on SKS-30) has on the minimum value of the coefficient of friction μ_m (curves 1, 2 and 3), and its influence on the true tensile strength σ of the stock (curve 4). 1. Friction of the rubber on steel. 2. On the aluminum alloy AMG. 3. On Plexiglas. The abscissa represents the number of parts of carbon black by weight per 100 parts of the polymer. The ordinate at left represents μ_m ; that at right the tensile strength in kg. per sq. cm.

by the load ($F_0 = A = \text{constant}$). Substituting Equation (2) in Equation (1), we get:

$$\mu = \mu_{\infty} + \frac{A}{N^k} \quad (3)$$

In order to verify the applicability of this equation⁷, it was necessary to plot the experimental data in terms of μ versus $1/N^k$, with the expectation that the points would lie on a straight line, the tangent of whose angle of slope would equal A .

TABLE I

VALUES OF THE CONSTANTS OF EQUATION (3) IN THE FRICTION OF RUBBER ON TEST-PIECES OF VARIOUS MATERIALS

Rubber	Filler	Parts by weight	k	Plexiglas		AMG-7		Steel-25	
				μ_{∞}	A	μ_{∞}	A	μ_{∞}	A
Natural rubber	None	0	0.30	0.57	350	0.50	330	0.43	230
	Gas black	40	0.60	0.57	35	0.50	35	0.43	20
SKB-35	None	0	0.30	0.46	370	0.36	200	0.28	300
	Gas black	60	0.62	0.47	130	0.38	90	0.30	80
SKN-26	None	0	0.45	0.57	415	0.45	450	0.52	400
	Gas black	45	0.68	0.62	130	0.35	120	0.59	115
	Gas black	60	0.75	0.62	75	0.35	70	0.62	55
	Gas black	120	0.92	0.52	40	0.32	35	0.39	30
	Chalk	60	0.60	—	—	0.35	205	0.57	250
	Chalk	120	0.62	—	—	0.30	60	0.35	35
SKS-30	None	0	0.46	0.70	350	0.60	400	0.60	375
	Graphite	10	0.54	0.53	160	0.54	140	0.62	140
	Graphite	50	0.65	0.55	65	0.54	65	0.51	65
	Graphite	120	0.79	0.38	30	0.50	30	0.38	30
	Powdered silica gel	50	0.65	0.61	110	0.64	110	0.58	100
	Powdered silica gel	120	0.89	0.49	30	0.51	30	0.48	30
Neoprene	None	0	0.49	0.27	155	0.32	60	0.26	110
	Lamp black	50	0.70	0.27	90	0.32	20	0.24	35

Note: The quantity A is given for the case where N is measured in grams.

In order to achieve this, we expressed k in terms of the limits $0 < k < 1$. We took advantage of the fact that, according to GOST No. 263-41⁸, the hardness of rubber can be expressed in the units of an instrument (the Shore durometer) with a scale ranging from 0 to 100, on which all rubbers fall between limits of 20 and 99. We let k represent the Shore hardness divided by 100. This method, to be sure, is of an empirical nature. We had recourse to it by reason of the incompleteness of present-day knowledge of the hardness of materials, the mechanical properties of rubber, and friction. We must, however, ascertain to what extent its use is permissible in the range where it can be related to the phenomena mentioned. It is evident from Figure 1b that Equation (3) is satisfactory.

Analogous data have been obtained for friction on steel, on the aluminum-magnesium alloy AMG, and on Plexiglas of various rubber compounds based on different rubbers and loaded with graphite, whiting, carbon black, and silica. The constants of Equation (3) are shown in Table I. These data are found to

agree with values from the literature¹. The fact that μ_{∞} does not equal zero attests to the inaccuracy of Schallamach's theory² and of his equation $\mu = B \cdot N^{-1/2}$; his experimental data for this do not agree with his own equation, but instead they satisfy Equation (1) nicely.

Table 1 shows that the quantity A , which characterizes the adhesive forces between the rubber and the other test-piece, is determined basically by the nature of the rubber itself rather than by that of the other material. This is because rubber, being the softer material, adapts itself in almost the same way to the contours of all the various other test parts, whose hardness is many times greater than that of the rubber. There is only a tendency for A to increase as we go from harder to softer materials, in this order: steel, AMG alloy, Plexiglas.

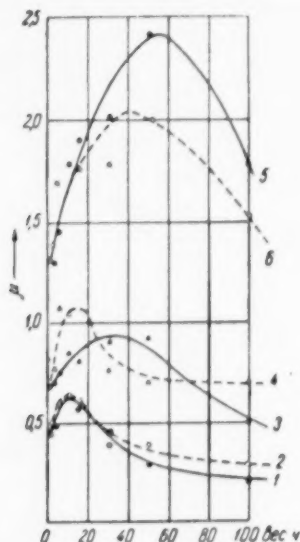


Fig. 3.—Influence of the quantity of plasticizer in the stock (based on SKN-26) on the coefficient of friction μ under various load pressures P . 1 and 2. $P = 10$ kg. per sq. cm. 3 and 4. $P = 1.3$ kg. per sq. cm. 5 and 6. $P = 0.1$ kg. per sq. cm. 1, 3, and 5. With dibutyl sebacate as the plasticizer. 2, 4, and 6. With triethylene glycol dibutyrate. The abscissa represents the number of parts of plasticizer; the ordinate the coefficient of friction μ .

This situation is revealed especially clearly when the hardness of the rubber is changed⁴; a decrease of the hardness increases A considerably, because of the increase of the area of actual contact. (The manner in which the hardness of the rubber is changed has almost no effect on this.)

The data in the table show that μ_{∞} does not change with the loading of the stock, if the filler is present in amounts within the limits of compatibility with rubber; i.e., when all the particles of the filler are surrounded by a layer of vulcanized rubber. Beyond these limits, when the particles of the filler form a layer between the rubber and the other test piece, μ_{∞} decreases. This conclusion is confirmed by the data of Figure 2, in which the tensile strength of the rubber starts to drop at the same filler concentrations where μ_{∞} decreases, since at this point the rubber in the stock becomes discontinuous in structure. The limits of compatibility are approximately the same, by volume, for all the fillers.

The effect of a plasticizer on friction may be considered analogous to that of a filler. Figure 3 shows that, up to the point where the plasticizer reaches the limit of compatibility with the rubber, i.e., when it swells but the plasticizer does not exude, the introduction of the plasticizer, by reducing the hardness, increases the coefficient of friction. This affects A but not μ_e ; i.e., it has an effect in the region of small loads (see Equation (3)). When the plasticizer exudes from the stock, however, it acts as a lubricant, and it also has the effect of reducing μ_e ; that is, it has an effect in the region of great loads as well. It is possible that the process of exudation (squeezing out) of the plasticizer is facilitated by large normal loads, which shift the threshold of compatibility.

When the quantities of softener used exceed the limits of compatibility, the friction can no longer be considered as dry friction, since μ depends directly on the duration of the stationary contact, and the data here do not coincide with Equation (3), which is accurate for friction without lubrication.

Hence these general conclusions: as long as the amounts of the compounding ingredients present in a rubber stock are within the limits of compatibility with rubber, the quantity μ_e (which plays its part when the loads are large) is independent of the ingredients present. This quantity is determined only by the interaction between the layer of rubber and the other test material. The hardness of the rubber, which depends on the amounts and nature of the ingredients (fillers and plasticizers) present, affects the quantity F_0 (and thereby the constant A), and plays its part when the loads are small.

The authors thank B. V. Deryagin for his discussion.

REFERENCES

- ¹ Ratner, *Doklady Akad. Nauk SSSR* **83**, 3 (1952); Ratner and Sokol'skaya, *Doklady Akad. Nauk SSSR* **86**, 1 (1952); Ratner, *Doklady Akad. Nauk SSSR* **93**, 1 (1953).
- ² While this paper was being printed, a work was published (Bulgadnev, *Doklady Akad. Nauk* **97**, 5 (1954)) dealing with the relation between the force of static friction and the "elemental forces". In that paper, it was shown that the smoother the surface is, the greater is the part played by the elemental forces which arise between the materials in contact. These results strengthen the belief on which our work is based; there is only a difference in the terminology. That is, the "elemental forces" of friction are related to the molecular roughness (μ_1) which we had called microroughness (Ratner, *Doklady Akad. Nauk* **93**, 1 (1953), but which should, in fact, be called ultramicroroughness (Deryagin, "What is Friction?", *Ist. AN SSSR* 1952). This is because the term "microroughness" usually applies to a surface "the static friction of which can be demonstrated with the well-known model consisting of two files" (Bulgadnev, *Doklady Akad. Nauk SSSR* **97**, 5 (1954)). We had (Ratner, *Doklady Akad. Nauk SSSR* **93**, 1 (1953)) designated this latter (μ_2) as macroroughness, which is not acceptable since this term is applied to unevennesses which appear different to the naked eye.
- ³ Deryagin, Ratner and Futran, *Doklady Akad. Nauk SSSR* **92**, 6 (1953).
- ⁴ Ratner and Sokol'skaya, *Doklady Akad. Nauk SSSR* **86**, 1 (1952).
- ⁵ Deryagin, "What is Friction?", *Ist. AN SSSR* 1952.
- ⁶ Ratner, *Doklady Akad. Nauk SSSR* **83**, 3 (1952); Ratner and Sokol'skaya, *Doklady Akad. Nauk SSSR* **86**, 1 (1952); Ratner, *Doklady Akad. Nauk SSSR* **93**, 1 (1953); Deryagin, "What is Friction?", *Ist. AN SSSR* 1952; Kragel'skii, "Aggregate Friction and Boundary Lubrication", *IL* 1953, p. 3.
- ⁷ The influence of the hardness of the rubber and of the pressure P of the load, which was noted above, may be expressed by the equation: $F_0/N = f(x)$, where the non-dimensional quantity $x = E/P$ is related not to the hardness, but to a more definite physical quantity, namely, the modulus E . However all attempts to render this equation more concrete, in the form of $f(x) = x e^{-x}$, etc., have so far failed to give any results which agree with the experimental data.
- ⁸ "Rubber, Methods of Testing", 1947.
- ⁹ Schallamach, *Proc. Phys. Soc.* **65**, B, 658 (1951).

APPARATUS FOR THE CONTINUOUS MEASUREMENT OF STRESS RELAXATION IN VULCANIZED RUBBER *

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The measurement of stress relaxation in vulcanized rubber is based on the principle that, when kept at constant elongation, a stretched sample of rubber shows a progressive decrease of stress with time and that this decrease depends both on the nature of the compound and on the temperature of testing. The resultant curve is a decreasing potential, which is expressed approximately by the equation: $\sigma_t = \sigma_0 \cdot e^{-kt}$, where σ_t is the instantaneous stress at time t , σ_0 is the initial stress, and k is a reaction rate constant which depends on the free activation energy of the rubber chain molecules.

Tobolsky was the first to apply the relaxation theory to the study of the oxidation behavior of compounds and to the approximate determination of the nature of vulcanization structures¹.

Certain types of apparatus are available for the discontinuous measurement of this stress relaxation², but we have designed, with the aid of the French Rubber Institute technical service, a relaxometer for the continuous recording of this phenomenon.

Figure 1 shows a general view and Figure 2 a schematic diagram of the relaxometer. Essentially the apparatus is constituted of a beam scale with asymmetric arms mounted on a ball-bearing at A. The length ratio is 6/1. A device makes it possible to elongate the test-piece E and keep it at a determined elongation on a graduated column C between two clamps, M_{A_1} and M_{A_2} . M_{A_2} is locked with a block turning round axle (a) on a ball-bearing. As the test-pieces must not undergo any change of elongation with time, special clamps were chosen, which are designed from the clamps used for T-50 test measurements. The test-pieces were cut out with the same die as for this test, from sheets 1 mm. thick. The elongation may vary from 0 to 800 per cent.

The test-piece, clamps, and column assembly are enclosed in a heating chamber E.C., the temperature of which is regulated within 1° C by a Sunvic type power regulator, shown on the photograph at R. The resistance U, used for heating, is located so that the greatest heating is at the bottom of the chamber, in order to avoid inside the chamber a troublesome temperature gradient.

As soon as the test-piece is elongated, equilibrium is established by running the slide C along the worm-screw V opposite the graduations of the arm. Three slides are provided for different elongations, so as to balance any stress from 0 to 2 kg. The smallest division of the beam, used with the smallest slide, corresponds to 0.5 gram, but the sensitivity of the apparatus is considerably increased by an electric contact consisting of a curved platinum wire dipping into the mercury cup G.

Once the test-piece is stretched and equilibrium established, any decrease of stress will bring the platinum wire into contact with the mercury surface.

* From the *Revue Générale du Caoutchouc*, Vol. 32, No. 12, pages 1105-1107, (in English 1134-1136), December 1955.

This contact, through a transformer and a relay (see wiring diagram in Figure 3) will start two synchronous motors, Mo_1 and Mo_2 . The first one, by rotating the screw V mounted directly on its axis, will bring the slide back towards the axis of the beam, establishing equilibrium again instantaneously and opening the circuit by lifting the platinum wire. The vertical displacement of the end of the beam is not over 0.1 mm. Consequently the distortions of the test-piece, which are 6 times smaller, may be neglected.

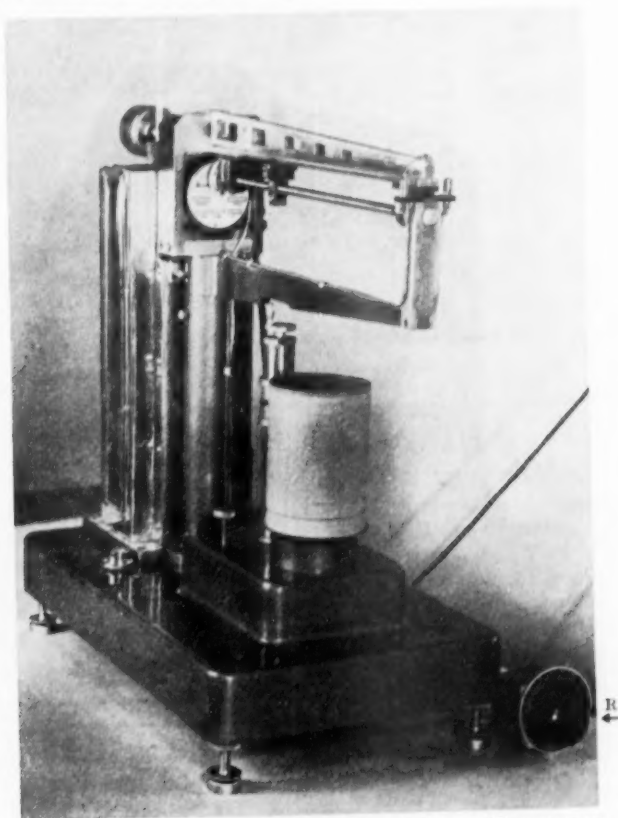


FIG. 1.—The relaxometer of the French Rubber Institute. (The instrument indicated by R is a regulator.)

The second motor Mo_2 is synchronized with Mo_1 , and, following exactly the impulses of the first motor, it causes vertical displacement of the stylus S on the recording drum T through the rotation of a screw located in the sleeve F . The drum, supplied with a timing device, turns around a vertical axle, so that the relaxation curve is recorded as a function of time. The stylus can be brought back to zero for each new determination through a disengaging system.

The screw assembled on Mo_1 is 32 cm. long, with a $\frac{1}{2}$ pitch. The motor speed is 8 r.p.m. The screw driven by Mo_2 is 16 cm. long, with the same pitch; the speed is 4 r.p.m.

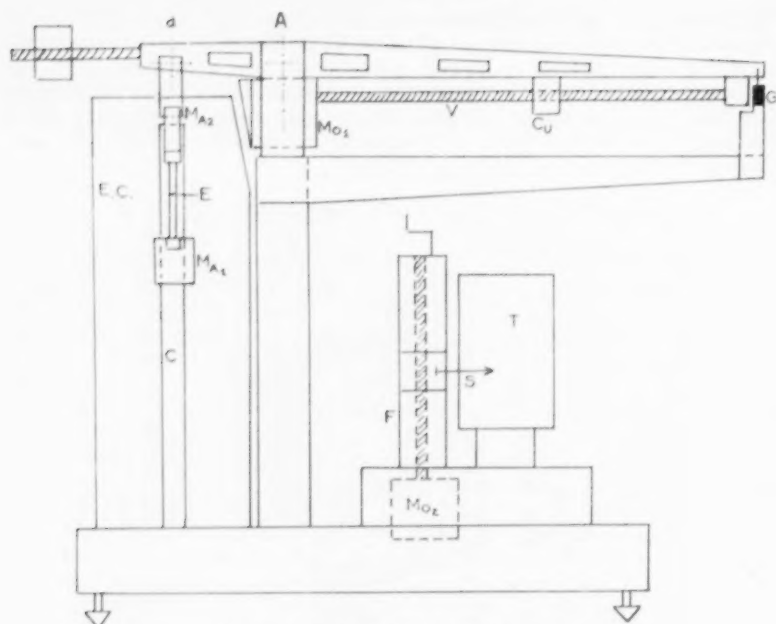


FIG. 2.—Schematic diagram of the relaxometer.

The dimensions of the unit are: height, 48 cm. (19 inches); length, 60 cm. (24 inches); width, 30 cm. (12 inches).

The curves obtained show an infinity of plateaus, which give them the appearance of continuous curves.

As an example, the photographs in Figure 4 show two curves obtained with this apparatus from the relaxation of two accelerated compounds, one by diphenylguanidine, the other by mercaptobenzothiazole.

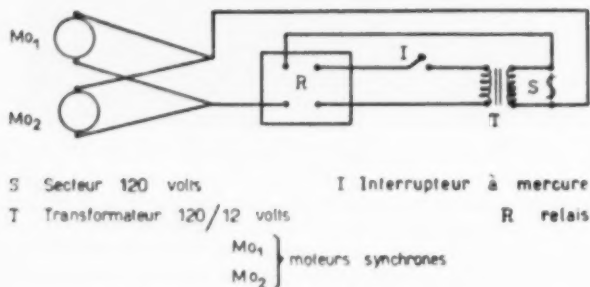


FIG. 3.—Diagram of the wiring of the relaxometer.

S—Electric supply (120 volts)
 T—Transformer
 R—Relay
 I—Mercury circuit breaker
 M_O1—Synchronous motors
 M_O2—Synchronous motors

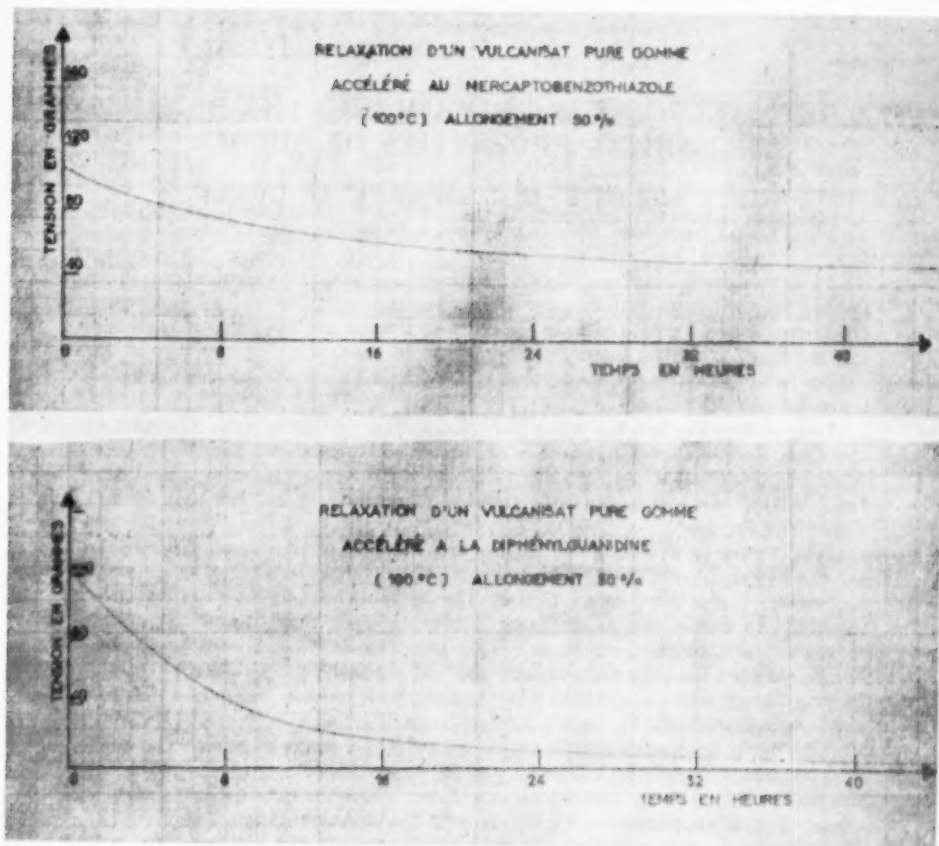


Fig. 4.—Relaxation of two pure-gum vulcanizates stretched 100 per cent at 100° C. The stress-time relation. The abscissa indicates the time in hours; the ordinate the stress in grams. Upper diagram—Vulcanizate accelerated with mercaptobenzothiazole. Lower diagram—Vulcanizate accelerated with diphenylguanidine.

Finally, let us point out that discontinuous stress measurements are also possible with this relaxometer, by stretching periodically the test-piece located in the heating chamber and determining the stress required to establish equilibrium again by moving slide C_0 on screw V by hand.

It is thus possible to measure the modulus at any given temperature. With such measurements, referred to continuous relaxation for a given compound, useful data can sometimes be deduced concerning the aging process and the action of protective agents.

This new relaxometer, an essentially theoretical laboratory apparatus, may thus be used for certain industrial applications, in particular for studying the protection of rubber.

REFERENCES

- ¹ Tobolsky, Prettyman, and Dillon, *J. Applied Physics* 15, 380 (1944).
- ² Tobolsky, Prettyman, and Dillon, *J. Applied Physics* 15, 380 (1944); Pedersen and Nielsen, *J. Polymer Sci.* 7, 97 (1951); Dogadkin and Tarasova, *RUBBER CHEM. AND TECHNOL.* 26, 759 (1953).

A NEW METHOD FOR DETERMINING THE DYNAMIC MECHANICAL PROPERTIES OF RUBBER *

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In submarines, machinery with reciprocating rotating parts is placed on rubber mountings to isolate noise and vibration from the hull of the vessel. Otherwise the hull would radiate the noise to the sea and facilitate detection of the submarine by the enemy. The dynamic mechanical properties of the rubber in the mountings determine to a large extent their effectiveness in isolating noise and vibration¹.

Only within the last ten years has reliable information become available on the dynamic mechanical properties of rubber at high frequencies of vibration. Most of this advance has been due to Nolle¹. Other workers in this field have been Witte, Mrowca and Guth², Hillier³, Cramer and Silver⁴, and Morris, James and Snyder⁵.

Nolle⁶ gave an excellent description and analysis of techniques for measuring the dynamic mechanical properties of rubber in the frequency range of 0.1 to 120,000 cycles per second (cps). The methods which he described were identified as rocking-beam oscillator, vibrating reed, strip transmission, strip resonance, and magnetostriction. Guth and associates, Hillier, and Cramer and Silver used the strip transmission method in their respective investigations. Morris, James, and Snyder used a bar transmission method which had not been previously described.

This paper deals with a modification of the bar transmission method, whereby the resonant frequency and dispersion of the vibrational energy above and below the resonant frequency are measured. From this information the velocity of sound, Young's modulus, and loss factor of the rubber are calculated.

THEORY

When a metal bar is clamped at both ends by exceedingly rigid and heavy clamps, and longitudinal vibrations are produced in the bar by suitable means, a longitudinal standing wave will occur in the bar at a certain frequency. This standing wave is $\frac{1}{2}$ wave length, and has an amplitude node at each end of the bar and an amplitude antinode at the center. The longitudinal velocity of sound in the bar can be calculated from the length of the bar and the frequency of resonance:

$$C_0 = 2LV_0 \quad (1)$$

where C_0 = velocity of sound in centimeters;

L = length of bar in centimeters;

V_0 = frequency in cycles per second at resonance.

Young's modulus of the bar can be calculated from the velocity of sound in the bar and its density:

$$E_1 = \rho C_0^2 \quad (2)$$

* Reprinted from the *Rubber Age* of New York, Vol. 78, No. 5, pag. 725-731, February 1956.

where E_1 = Young's modulus in dynes per square centimeter;
 p = density of metal in bar.

If the bar is rubber instead of metal, the phenomenon of resonance is more complicated, because rubber absorbs more vibrational energy than metal. This behavior of rubber is due to its higher internal viscosity. The effective modulus is no longer the modulus calculated from Equation (2), but is a value which takes into account the force necessary to overcome the viscous component in the rubber, as well as the force necessary to overcome the elastic component. Nolle termed this modulus the complex Young's modulus. He gave the following relationship (using complex numbers) between the complex modulus, the real modulus representing the elastic component, and the so-called imaginary modulus representing the viscous component:

$$E^* = E_1 - iE_2 \quad (3)$$

where E^* = complex Young's modulus;
 E_1 = real or ordinary Young's modulus;
 E_2 = imaginary Young's modulus.

The real and imaginary moduli were calculated from the following equations:

$$E_1 = \frac{pC_0^2(1-r^2)}{(1+r^2)^2} \quad (4)$$

$$E_2 = \frac{2rE_1}{1-r^2} \quad (5)$$

where $r = 0.776 \frac{\Delta V}{V_0}$, and

ΔV = band width in cycles per second, measured between the two frequencies for which the amplitude of vibration was $1/\sqrt{2}$ times the amplitude at V_0 (see Figure 1).

Nolle stressed the importance of the ratio E_2/E_1 , which he termed the loss factor. He pointed out that the loss factor is a means of classifying rubbers according to their potentialities as practical absorbers of mechanical energy. The loss factor is a measure of the damping of an oscillating system composed of a rubber sample attached to a rigid surface at one end and to a freely oscillating mass at the other end, such as a machine supported on rubber mountings. The damping of such a system is related to the loss factor of the rubber in the mounting by the following equation:

$$\log_e \frac{y_0}{y_1} = \frac{E_2}{E_1}$$

where y_0 = amplitude of one cycle of free vibration, and
 y_1 = amplitude of following cycle of free vibration.

Harrison, Sykes and Martin⁷ pointed out that the sound velocity calculated from Equation (1) is not exact if the diameter of the cylindrical test-specimen is an appreciable fraction of the longitudinal wave length in the specimen. In this case the sound velocity, C , is less than the sound velocity, C_0 , which would be calculated from Equation (2).

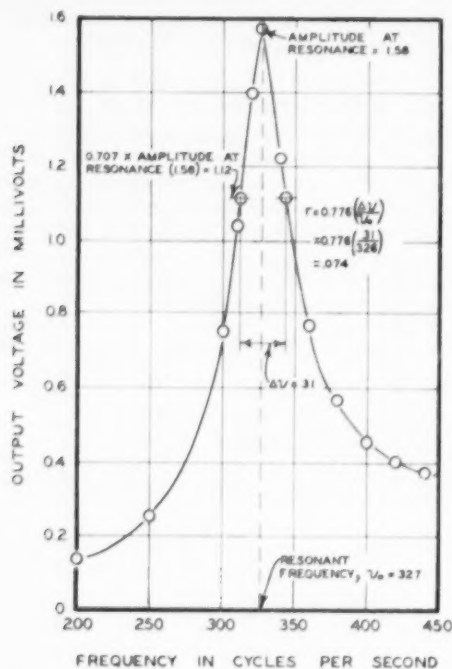


Fig. 1. Resonant peak for natural-rubber gum specimen, showing method of finding the band width, ΔV .

Figure 2 is a reproduction of a portion of the curve given by these authors for obtaining the ratio, C/C_0 , from the ratio of the specimen diameter, d , to the wave length, λ . In the present work the uncorrected velocity was calculated from Equation (1), using the measured values of specimen length ($\frac{1}{2}\lambda$), and the corrected velocity obtained from the ratio given in Figure 2 was used in Equation (4) to calculate the real modulus.

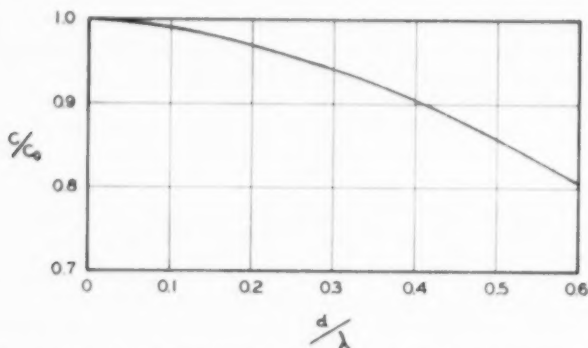


Fig. 2. Ratio of longitudinal wave velocity in a cylinder to the Young's modulus velocity as a function of diameter to wave length ratio d/λ .

DESCRIPTION OF APPARATUS

The test apparatus consisted of two parts: the specimen holder and the associated electronic equipment. The specimen holder comprised a very heavy rectangular solid steel frame with two cylindrical piezoelectric transducers mounted face to face on the inside of the frame. One of the transducers was threaded into the center of the lower cross-piece of the frame. The other was threaded into the end of a plunger, which passed through the center of the upper cross-piece. The plunger itself was threaded and provided with two locknuts for rigidly positioning the upper transducer.

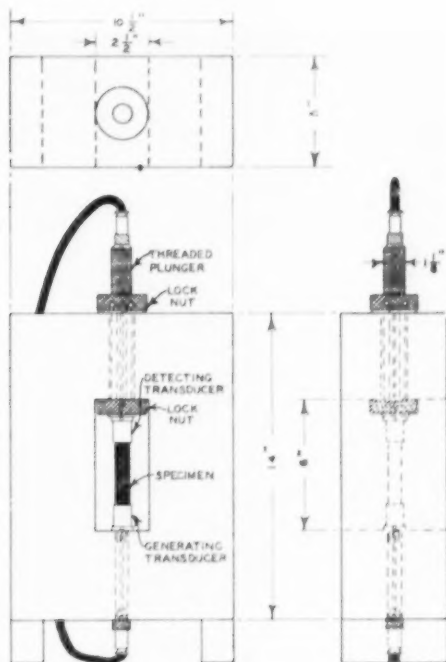


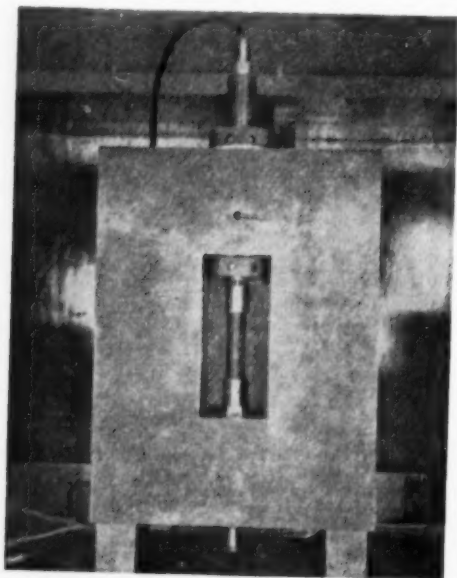
FIG. 3.—Drawing of specimen holder.

The frame was supported by two legs to provide clearance for the cable going through the lower cross-piece into the lower transducer. The cable to the upper transducer was admitted through the hollow plunger. The specimen holder was isolated from outside vibrations by mounting it on a slab of felt one inch thick. The specimen holder, with specimen in position, is illustrated in Figure 3 and the photograph in Figure 4.

The transducers in the specimen holder were actually accelerometers*. Each consisted of a sandwich of six ammonium dihydrogen phosphate (ADP) crystal plates, mounted within a stainless steel housing one inch in diameter and about one inch long. The housing was closed with a metal cap, which had on its outer face a concentric cavity 13/16 inch in diameter and 3/64 inch deep. The cap was about 0.010 inch thick at the bottom of the cavity and was

cemented to the end of the crystal assembly. The other end of the crystal assembly was cemented to the base of the accelerometer.

When testing, a cylindrical rubber specimen, $\frac{1}{4}$ inch in diameter, was clamped between the two transducers. The generating (lower) transducer was made to vibrate in a vertical direction by applying alternating current at 500 volts to the crystals. This impressed a longitudinal vibration on the rubber specimens. The amplitude of vibration at this voltage was approximately 5×10^{-6} inch². The alternating current was obtained from an audio-signal generator through a step-up transformer. The voltage was monitored with a vacuum-tube voltmeter, and the exact frequency of alternations was read from a frequency counter.



4. The specimen holder is isolated from outside vibrations by mounting it on a slab of felt one inch thick.

The voltage produced in the detecting (upper) transducer by the longitudinal vibrations in the rubber specimen was passed through a cathode follower, amplified, and measured with a vacuum-tube voltmeter. The wave forms of the generated and detected signals were observed with an oscilloscope. A block diagram of the entire system is shown in Figure 5, and a photograph of the apparatus excepting the frequency counter in Figure 6.

DETAILS OF OPERATION

The reason for the very heavy construction of the specimen holder frame was to limit the resonances in the frame to high frequencies. These resonances would otherwise have interfered with the determination of the resonant frequencies of the rubber specimens. Figure 7 is a plot of the voltage from the detecting transducer when the generating transducer was driven with 500 volts at various frequencies with no rubber specimen between the transducers. It

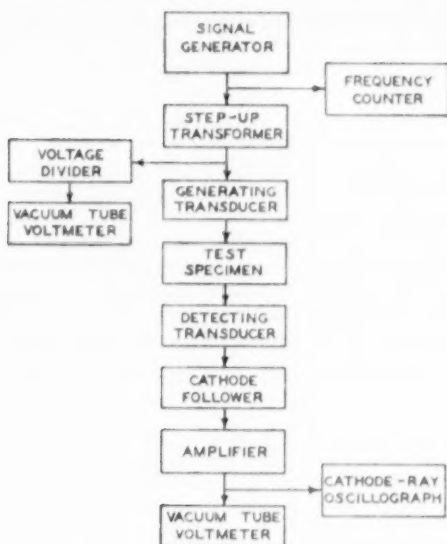


Fig. 5.—Schematic diagram of apparatus.

will be noted that the first resonance in the specimen holder occurred at 3280 cps, and that the disturbance from this resonance would not interfere with the determinations of resonances in rubber specimens at frequencies below 3000 cps. This was to be expected.

It was intended that a rubber specimen being tested would resonate at $\frac{1}{2}$ wave-length with the amplitude nodes at the ends of the specimen. In order for this to take place, it was required that the ends of the specimen bear against exceedingly rigid surfaces to reflect the sound wave. The ADP crystals in

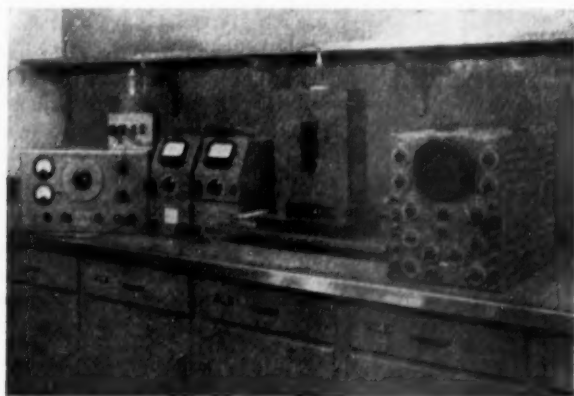


Fig. 6.—Test apparatus (frequency counter not shown).

the transducers had a Young's modulus of about 10×10^{10} dynes per sq. cm. This was sufficiently greater than the Young's modulus of rubber, the range of which is 10×10^6 to 1000×10^6 dynes per sq. cm., for the transducers to serve as efficient reflectors.

It was proved that the rubber specimen being tested resonated at $\frac{1}{2}$ wave length with the amplitude nodes at the ends of the specimen. A natural-rubber gum specimen, nominally 2.75 inches long, was placed between the transducers and compressed 2 per cent. The generating transducer was driven at 500 volts, and the alternating frequency of the current was gradually increased until resonance occurred in the rubber specimen, as indicated by a peak in the signal from the detecting transducer. While resonance was maintained, the longitudinal movement of the surface of the specimen at various points along its length was surveyed with a phonograph pickup. The signal from the pickup was observed on an oscilloscope. The signal had a maximum value when the needle

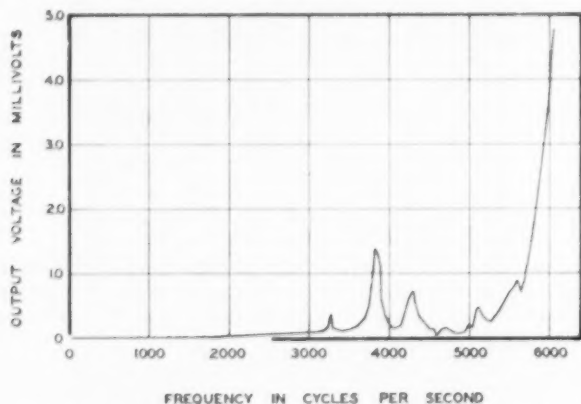


Fig. 7.—Voltages at detecting transducer when rubber specimen was not clamped between transducers.

of the pickup was pressed lightly against the rubber specimen midway between the transducers. The signal decreased when the needle was moved toward either transducer and reached a minimum value next to the transducers.

This testing method employed measurements of specimen length, resonant frequency, and band width to determine the dynamic mechanical properties of rubbers. Since the resonant frequency of a rubber specimen was directly related to its length, specimens of different lengths were needed to determine dynamic properties at different frequencies. The length of the specimens, however, could not be varied over a very wide range, because the inside dimensions of the frame limited the maximum specimen length to 2.75 inches, and the undesirability of a standing wave in the transverse direction limited the minimum specimen length to 0.75 inch. In view of these limitations of specimen length, the frequencies at which the dynamic properties of any given vulcanizate could be determined, could not be varied by a factor greater than about 3.7.

EFFECTS OF VARIOUS TEST CONDITIONS

When establishing the test procedure, it was necessary to decide upon certain conditions, namely, the treatment of the ends of the test-specimens, the

degree of compression during test, and the duration of compression before starting measurements.

It was felt that the resonant frequency would not be affected significantly by the degree of bearing friction between the rubber specimen and the transducers. This followed from the fact that the ends of the rubber specimen were nodes when resonance occurred, and therefore were essentially stationary. Bearing friction was proved to have no effect on resonant frequency by a series of measurements using the same rubber specimens and different degrees of friction between the specimens and the transducers.

The same resonant frequencies, within experimental error, were obtained when measurements were made with discs of fine-grit sandpaper between the specimen and the transducers (rough surface against rubber), with clean and dry surfaces, with surfaces lubricated with silicone grease, and with the surfaces lubricated with silicone oil. It was decided to use silicone grease in subsequent measurements to guarantee good contact between the ends of the rubber specimens and the transducers.

TABLE I
EXPERIMENTAL DATA FOR NATURAL RUBBER SPECIMEN, $P = 6.978$,
 $L = 7.05$ CM., TESTED AT VARIOUS COMPRESSIONS

Comp. (%)	Amplitude at Resonance (mv)	λ (cm.)	V_R (cps)	ΔV (cps)	C_R (cm./sec.)	E_1 (dynes/cm. ²)	E_2 E_1
1.8	1.58	13.85	327	31	4620	20.6×10^8	0.15
6.4	1.53	13.31	346	34	4660	20.9×10^8	0.15
10.0	1.48	12.70	359	36	4650	20.8×10^8	0.16
13.6	1.37	12.19	385	37	4790	22.1×10^8	0.15
17.2	1.32	11.68	405	42	4830	22.5×10^8	0.16

To find the effect of compressing the rubber specimen on its dynamic properties, a natural-rubber gum specimen approximately 2.75 inches long was tested at various compressions ranging from 1.8 to 17.2 per cent. The ambient temperature was held at 74° F. The results of the tests are given in Table I. As the compression of the specimen increased, its amplitude of vibration (voltage at detecting transducer) at resonance decreased. Up to 10 per cent compression there was little if any effect on sound velocity, real modulus or loss factor. From 10 to 17.2 per cent compression, sound velocity and real modulus increased somewhat. It was decided to standardize on 2 per cent compression for future measurements at room temperature unless the effect of compression itself was being investigated.

The effect of elapsed time between compressing the specimen and testing was determined, using natural rubber and Thiokol-FA gum specimens, approximately 1.75 inches long and held at 2 and 6 per cent compression. The measured properties, sound velocity and band width, were unchanged within experimental error when the compression time was extended from 15 minutes to one hour. A compression time of at least 15 minutes before the measurements was adopted for subsequent tests.

PRECISION OF TEST RESULTS

The precision or reproducibility of the results of this test was found by performing tests on the same natural-rubber gum specimen at random intervals in a period of four months. A total of 14 tests was made. The specimen was

approximately 2.75 inches long and was compressed 2 per cent, at an ambient temperature of $73.5^{\circ} \pm 1^{\circ}$ F during the tests. The statistical information obtained for the two measured values, resonant frequency and band width, is given below.

	Resonant frequency V_s	Band width ΔV
Highest value (cps)	338	32
Lowest value (cps)	324	28
Average value (cps)	330	30
Average deviation (cps)	2.9	0.9
Maximum deviation (cps)	8.0	2.0
Standard deviation (cps)	3.7	1.2
Coefficient of variation (%)	1.1	4.0

The foregoing data show that the results had excellent precision.

SOME EXPERIMENTAL RESULTS

Tests over range of frequencies.—Figure 8 illustrates the signals received by the detecting transducer when specimens approximately 2.75 inches long and compressed 2 per cent were tested over the range of frequencies of 0 to 1400 cps. The signals received through a natural-rubber gum specimen and a Butyl gum specimen are shown. The natural rubber specimen exhibited a very sharp resonance at 327 cps and progressively less sharp resonances at 638 and 903 cps. These peaks corresponded to standing waves of $\frac{1}{2}$, 1 and $1\frac{1}{2}$ wave lengths, respectively. The frequency of the standing wave containing a full wave length was not exactly twice that of the first standing wave, as would be the case in a metal bar, because the velocity of sound in the rubber increased with frequency.

The Butyl-rubber specimen had a very flat resonance at about 900 cps. This characteristic was due to the very high internal viscosity of Butyl rubber. Accurate calculations of dynamic properties could not be made from this curve.

Tests of various gum vulcanizates.—Test-specimens were prepared from the eight stocks formulated in Table II. Test-specimens of each stock were prepared with the following approximate lengths: 0.75, 1.25, 1.75, 2.25 and 2.75 inches. The dynamic mechanical properties of these specimens at 2 per cent compression and an ambient temperature of $73.5^{\circ} \pm 1^{\circ}$ F are given in Table III.

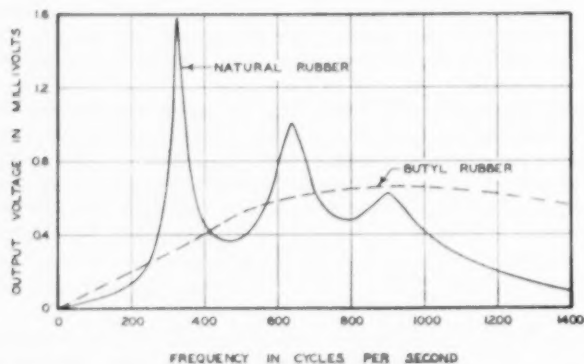


Fig. 8.—Resonance in 2.75-inch specimens of natural rubber and Butyl rubber gum stocks

Analysis of the data in Table III showed that, over the attainable frequency span for each stock, the following relationships prevailed.

(1) Sound velocity, real modulus, and loss factor tended to increase with frequency for all of the stocks.

(2) Natural rubber had the lowest sound velocity, lowest real modulus, and lowest loss factor of any of the rubber tested. The only exception to the foregoing was the slightly lower loss factor of GR-S 1023 around 1000 cps.

(3) GR-S 1015 had the lowest sound velocity and the lowest real modulus of the four GR-S polymers tested, and GR-S 1023 had the lowest loss factor.

(4) Thiokol-ST had somewhat lower sound velocity and somewhat higher real modulus than GR-S 1015, and considerably higher loss factor.

(5) Hycar-1014 and Neoprene-GRT had high sound velocities, high real moduli, and high loss factors.

TABLE II
RECIPES FOR GUM STOCKS

	Natural rubber	GR-S 1000	GR-S 1015	GR-S 1023	GR-S 1500	Thiokol- ST	Hycar- 1014	Neoprene- GRT
Smoked sheet	100.0							
GR-S 1000		100.0						
GR-S 1015			100.0					
GR-S 1023				100.0				
GR-S 1500					100.0			
Thiokol-ST						100.0		
Hycar-1014							100.0	
Neoprene-GRT								100.0
Pelletex	2.0							
Protex-166	5.0	5.0	5.0	5.0	5.0	0.5	5.0	5.0
XLC Magnesia								7.0
Stearic acid	1.0	1.0	1.0	1.0	1.0	3.0	1.0	1.0
Califlux-510	3.0							
Neozone-D	1.0							
Antioxidant-2246	1.0							
Altax	1.0							
Thionex	0.3	0.3	0.3	0.3	0.3			
Methyl Tuads							1.4	
Sulfur	1.5	1.8	1.8	1.8	1.8		0.8	
GMF						1.5		
Vulcanization (min. ° F)	65/290	65/290	65/290	65/290	65/290	70/270	70/280	30/310*
Density (p)	0.978	0.997	0.966	0.976	1.005	1.298	1.005	1.330

* Followed by 120/310° F in open steam and 24 hrs./212° F in air.

Tests of loaded stocks.—Specimens approximately 2.75 inches long were prepared from natural-rubber stocks loaded with 10, 20, and 30 volumes of the following materials per 100 volumes of rubber: Circo light process oil, Thermax medium thermal black, Shawinigan acetylene black, Miconex medium processing channel black, and Philblack-E superabrasion furnace black. The basic recipe for these stocks was the same as the pure-gum recipe given in Table II. The results of tests on these specimens are given in Table IV.

Adding 10 volumes of oil to the natural rubber stock brought about reductions in sound velocity, real modulus, and loss factor. Further additions of oil caused greater reductions of sound velocity and real modulus, but the loss factor rose to a value about equal to that of the gum stock.

The addition of the carbon blacks resulted in increases of sound velocity, real modulus, and loss factor. Medium thermal black caused less change of these properties than did the other blacks. Acetylene black and channel black produced about the same changes in sound velocity and real modulus. The loss factors of vulcanizates containing the latter three blacks were about the same (0.22 to 0.26) at all black loadings. This latter finding indicated that

TABLE III
 RESULTS OF TESTS ON VARIOUS GUM SPECIMENS

Rubber	Resonant frequency V_0 (cps.)	Corrected velocity C_v (cm./sec.)	Real modulus E_1 (dynes/cm. ²)	Loss factor E_2/E_1
Natural	332	4650	21×10^6	0.14
	414	4790	22×10^6	0.15
	527	4820	22×10^6	0.20
	726	4950	23×10^6	0.24
	1178	5100	23×10^6	0.32
GR-S 1000	472	6580	40×10^6	0.30
	583	6720	42×10^6	0.33
	746	6810	42×10^6	0.34
	1043	7090	45×10^6	0.39
	1736	7550	49×10^6	0.47
GR-S 1015	365	5120	24×10^6	0.28
	457	5270	25×10^6	0.33
	596	5440	26×10^6	0.34
	854	5800	30×10^6	0.36
	1368	5930	31×10^6	0.38
GR-S 1023	473	6630	41×10^6	0.24
	581	6740	42×10^6	0.27
	759	6940	44×10^6	0.26
	1045	7130	47×10^6	0.28
	1735	7880	56×10^6	0.33
GR-S 1500	422	5880	33×10^6	0.29
	521	5990	33×10^6	0.33
	679	6190	34×10^6	0.38
	960	6530	37×10^6	0.45
	1530	6630	41×10^6	0.52
Thiokol-ST	359	5030	29×10^6	0.45
	437	5070	29×10^6	0.47
	582	5340	32×10^6	0.47
	765	5260	30×10^6	0.51
	1312	5950	38×10^6	0.53
Hycar-1014	475	6680	40×10^6	0.42
	609	7020	43×10^6	0.46
	765	7070	42×10^6	0.52
	1180	7867	49×10^6	0.63
	1848	8200	48×10^6	0.76
Neoprene-GRT	461	6470	43×10^6	0.67
	573	6670	43×10^6	0.75
	779	7160	44×10^6	0.92
	1082	7400	44×10^6	1.01
	1775	8080	46×10^6	1.18

these carbon blacks caused the imaginary modulus to increase at the same rate as the real modulus when the black loading was raised from 10 to 30 volumes. In this connection, it would be interesting to know the loss factors at loadings below 10 volumes, because somewhere in this region the loss factor must drop from 0.22 to 0.14, the value for the gum stock.

TABLE IV
RESULTS OF TESTS ON SPECIMENS OF NATURAL-RUBBER
STOCKS LOADED WITH VARIOUS MATERIALS
(2.75-inch specimens)

Loading material	Loading (vols. per 100 vols. rubber)	Density, P (g./cm. ³)	Reso- nant fre- quency V_0 (cps)	Cor- rected velocity C_0 (cm./sec.)	Real modulus E_1 (dynes/cm. ²)	Loss factor E_2/E_1
None	0	0.978	332	4650	21×10^8	0.14
Circo-LP Oil	10	0.973	299	4170	17×10^8	0.12
	20	0.971	274	3810	14×10^8	0.15
	30	0.969	250	3470	12×10^8	0.14
Thermax (MT black)	10	1.053	364	5090	27×10^8	0.13
	20	1.113	406	5680	35×10^8	0.16
	30	1.167	454	6360	46×10^8	0.19
Shawinigan (Acetylene black)	10	1.050	543	7590	59×10^8	0.20
	20	1.109	917	12840	176×10^8	0.23
	30	1.160	1546	21740	529×10^8	0.22
Micronex (MPC black)	10	1.053	493	6900	48×10^8	0.22
	20	1.111	955	13460	193×10^8	0.25
	30	1.159	1540	21750	528×10^8	0.23
Philblack-E (SAF black)	10	1.051	555	7750	61×10^8	0.22
	20	1.108	1274	17860	337×10^8	0.26
	30	1.164	1945	27270	832×10^8	0.24

Tests at various temperatures.—The specimen holder was placed in a refrigerated cabinet, which could be held at any desired temperature below room temperature. The natural-rubber gum specimen and the Neoprene-GRT gum specimen, each approximately 2.75 inches long, were tested at 75°, 50°, 30°, 10°, and -10° F, in the range of frequencies 0 to 1400 cps. The compression of the specimens was adjusted to 6 per cent at room temperature to allow for thermal contraction at the lower temperatures, and thus bring the compression close to 2 per cent at these temperatures. At each temperature, the specimens

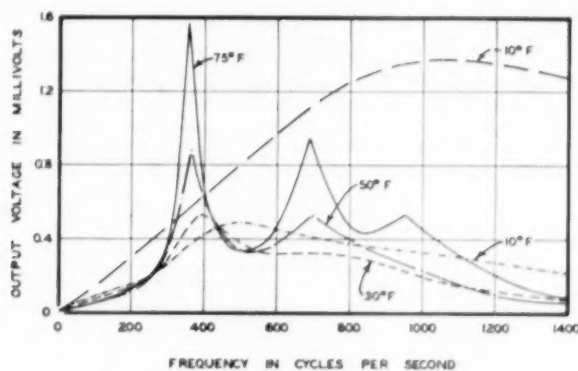


FIG. 9.—Resonances in 2.75-inch specimens of natural rubber gum stock at various temperatures.

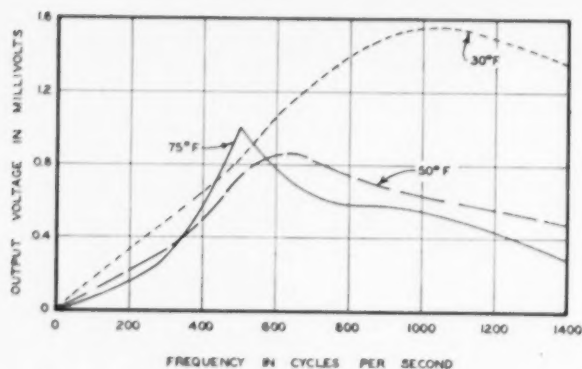


FIG. 10.—Resonances in 2.75-inch specimens of Neoprene GRT gum stock at various temperatures.

were conditioned only for the length of time needed to attain the temperature, since it was desired to avoid crystallization. The conditioning time was determined by means of a dummy specimen with an embedded thermocouple. The approximate time for temperature equilibrium was 35 minutes.

The transmission curves are given in Figures 9 and 10. As the temperature decreased, the internal viscosities of the rubbers increased, so the resonance peaks became less pronounced. At 50° F the $1\frac{1}{2}$ wave length resonance of the natural-rubber specimen was not found. At 30° F, the 1 wave-length resonance was barely noticeable. At 10° F, only the $\frac{1}{2}$ wave-length resonance was obtained, and it was flat. At -10° F, there was a great increase of amplitude at resonance, but the resonance peak was very flat because of high internal viscosity. The latter behavior was probably a manifestation of the onset of the second-order transition at these high frequencies.

In the case of the Neoprene specimen, no resonances other than that for the $\frac{1}{2}$ wave length were observed at any of the temperatures. The resonance peak was flat at 50° F, and at 30° F the peak was even less pronounced but had a high amplitude. This latter behavior was similar to that of the natural-rubber specimen at -10° F.

The dynamic mechanical properties of these specimens at the various temperatures are tabulated below. These data show that the real modulus of both stocks decreased as the temperature was lowered, but the loss factor increased greatly.

Rubber	Temp. (° F)	Reso- nant fre- quency V_s (cps)	Cor- rected velocity C_s (cm./sec.)	Real modulus E_1 (dynes/ cm. ²)	Loss factor $\frac{E_2}{E_1}$
Natural	75	356	4680	21×10^8	0.15
	50	363	4780	21×10^8	0.30
	30	391	5140	17×10^8	0.84
	10	500	6580	5×10^8	5.40
Neoprene	75	500	6750	46×10^8	0.68
	50	629	8490	33×10^8	1.91
	30	1071	14460	10×10^8	14.80

The decrease of real modulus with temperature is in line with the theory that the elastic property of rubber is an entropy effect¹⁰.

DISCUSSION

The only published information that is comparable to any of the data reported here is that given by Nolle¹¹ for a natural-rubber gum vulcanizate. By interpolating the curves which he gave for real modulus and loss factor at 50° F, the following comparison is made at a frequency of 363 cps.

	Real modulus E_1 (dynes/cm. ²)	Loss factor E_2 E_1
Nolle	26×10^8	0.31
Present work	21×10^8	0.29

This is considered to be good agreement, particularly since Nolle's stock contained 5 parts of sulfur and no softener, whereas the authors' stock contained only 1.5 parts of sulfur and 3 parts of softener. Nolle's stock would be expected to have higher modulus and loss factor because of these differences in composition.

This method of measuring the dynamic properties of rubber has the advantages of convenience and good precision, at least in the case of specimens with a low loss factor. Its principal disadvantages are its limited frequency range and the need for specimens of different lengths to obtain dynamic properties at desired frequencies. It is believed that this method is particularly suitable for specification testing of rubber vulcanizates to be used in mountings intended for isolating the sound of machinery.

ACKNOWLEDGMENTS

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REFERENCES

- ¹ Nolle, *J. Appl. Phys.* **19**, 753 (1948); *J. Polymer Sci.* **5**, 1 (1950).
- ² Witte, Mrowca, and Guth, *J. Appl. Phys.* **20**, 481 (1949).
- ³ Hillier, *Trans. Inst. Rubber Ind.* **26**, 64 (1950).
- ⁴ Cramer and Silver, U. S. Naval Ordnance Laboratory Rept. No. 1778 (February 1951).
- ⁵ Morris, James, and Snyder, *Ind. Eng. Chem.* **43**, 2540 (1951).
- ⁶ Nolle, *J. Appl. Phys.* **19**, 753 (1948).
- ⁷ Harrison, Sykes, and Martin, *J. Acoust. Soc. Amer.* **24**, 62 (1952).
- ⁸ Made by the Massa Laboratories, Inc., Hingham, Mass.; Massa, *Instruments*, **21**, 1012 (1948).
- ⁹ According to Massa, F., private communications.
- ¹⁰ Meyer, "Natural and Synthetic High Polymers", Interscience Publishers, Inc., New York, N. Y., 1942, p. 149.
- ¹¹ Nolle, *J. Polymer Sci.* **5**, 1 (1950).

THE HARDNESS OF VERY SOFT RUBBERS *

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Hardness determinations are frequently required on very soft rubbers in the range of 5 to 30 (Shore). It is usual to make such measurements in the shop with a pocket-type tester; however this is not entirely satisfactory for laboratory work where a more precise reading is usually required, calling for a hardness tester of the dead-load type. Such a tester, moreover, is useful to keep a check on the accuracy of pocket testers.

The British Standard dead-load hardness tester is not calibrated below 30° BS, but a method of extending the range downwards has been proposed¹, whereby the standard indenter of this tester is replaced by one of 0.25 inch diam.; unfortunately this method has the disadvantage of involving more than one revolution of the dial gauge needle, and a directly calibrated scale would be out of the question. There is, however, an alternative method in use at BRPRA, which gives hardness readings down to 4° in one revolution; and which replaces the standard added load of 535 grams by one of 70 grams. At present, a calibration curve is provided to convert from scale reading to hardness degrees, but it is intended to add a second scale in due course.

BRITISH STANDARD HARDNESS

The British Standard hardness scale is described in BS 903: 1950, and is elaborated elsewhere by Scott².

Briefly it is based on Scott's experimentally obtained relationship³ between the penetration of a spherical ball into the rubber surface and Young's modulus of the rubber; a mathematical device (the "probit" or integrated error function) is used to convert Young's modulus into British Standard hardness degrees. For a given set of conditions (diameter of indenter and load), a table may be drawn up to show the hardness in BS degrees corresponding to a range of indentations, and this table may be used either to draw a calibration curve or to construct a scale reading directly in BS degrees.

The standard conditions are an added load of 535 grams, and an indenter of diameter 3/32 inch; a calibrating table for these conditions is given in BS 903: 1950. This table is restricted to the range of 30–100° BS, since Scott's relationship does not hold for penetrations of more than 80 per cent of the indenter diameter, which, for the standard conditions, corresponds to the lower limit of the range of calibration, that is 30° BS.

The scale is arranged so that, like the Shore durometer, a low reading indicates a soft rubber, and a high reading a hard rubber, and gives, in fact, readings which are similar to those that would be given by a Shore durometer in perfect condition.

* Reprinted from the *Rubber Journal*, Vol. 130, No. 3, pages 70–71, January 21, 1956.

MEASURING HARDNESS

Dead-load hardness testers are of two types: those which actually measure the depth of penetration, usually in hundredths of a millimeter and require a calibration table or curve to convert to hardness degrees, and those which are directly calibrated in hardness degrees.

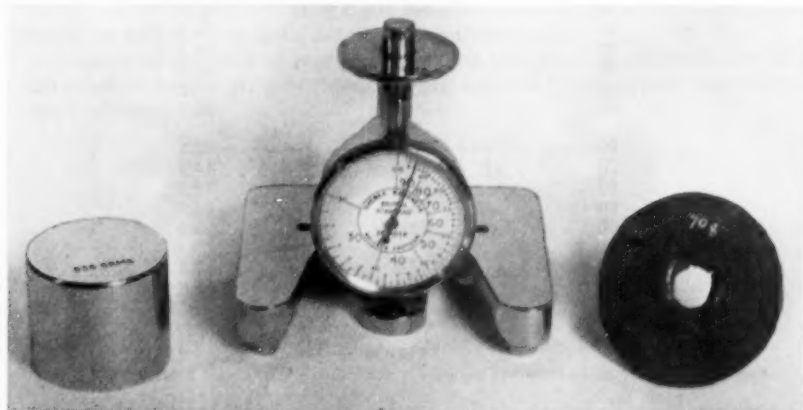


FIG. 1.—(a): The Wallace RABRM pattern gauge with (left) standard 535 grams and (right) special 70 grains major loads.

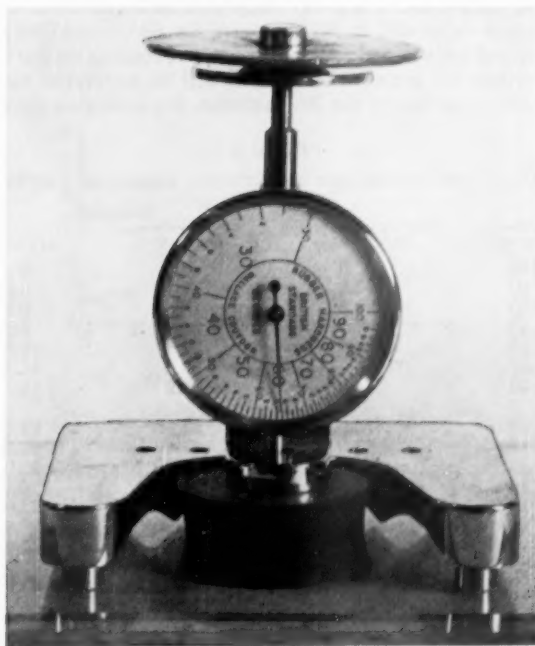


FIG. 1.—(b): The modified gauge in use; the reading of 65 is equivalent to an actual hardness of 16.5 degrees.

TABLE 1
RELATIONSHIP BETWEEN INDENTATION OF A $\frac{1}{16}$ INCH DIAMETER BALL
UNDER AN ADDED LOAD OF 70 GRAMS AND HARDNESS DEGREES

Indentation		Hardness (degrees)
(mm./100)	(in./1000)	
0	0	100.0
10	3.9	64.4
20	7.9	44.4
30	11.8	33.0
40	15.7	25.7
50	19.7	20.7
60	23.6	17.1
70	27.6	14.3
80	31.5	12.2
90	35.4	10.6
100	39.4	9.2
120	47.2	7.2
140	55.1	5.8
160	63.0	4.7
180	70.9	3.9
200	78.7	3.3

Note.—Theoretical considerations will not allow a penetration greater than 0.2 mm. (0.0787 in.).

In either case, the indenter is pressed into the rubber for five seconds under a load of 30 grams (the minor load), and the bezel of the gauge turned so that the pointer indicates zero for a gauge calibrated in hundredths of a millimeter or 100 for a gauge calibrated in BS degrees. An additional load of 535 grams is then applied and maintained for 30 seconds; the reading on the dial after this time will be either the penetration (which will be converted to hardness by means of a table or curve), or the BS hardness, depending on the scale used.

TABLE 2
DATA FOR CALIBRATING AN EXISTING HARDNESS TESTER

Hardness (degrees)	Existing scale reading (B.S. degrees)	Indentation	
		(mm./100)	(in./1000)
100	100.0	0	0
60	95.3	11.7	4.6
50	92.5	16.5	6.5
40	87.7	23.3	9.2
35	84.2	27.8	11.0
30	80.4	33.6	13.2
25	75.8	41.2	16.2
20	70.0	51.7	20.4
18	67.0	57.1	22.5
16	64.0	63.6	25.0
14	60.5	71.5	28.1
12	56.7	81.3	32.0
10	52.0	93.9	37.0
9	49.3	101.7	40.0
8	47.0	110.9	43.7
7	43.8	122.2	48.1
6	40.0	136.0	53.5
5	37.0	153.7	60.5
4	33.0	177.4	69.8

VERY SOFT RUBBERS

The method used in these laboratories for the measurement of the hardness of very soft rubbers is similar to that described above, except that the additional load is reduced from 535 to 70 grams, the minor load of 30 grams being retained.

A Wallace RABRM pattern gauge has been adapted for this purpose (Figure 1). The 70-gram weight is made by cutting disks from lead sheeting, and should be within $70(\pm 0.05)$ grams for accurate results.

Because of the reduced load in use for this method, it is necessary that the dial gauge be kept in good mechanical repair and free from dirt; adequate vibration is essential.

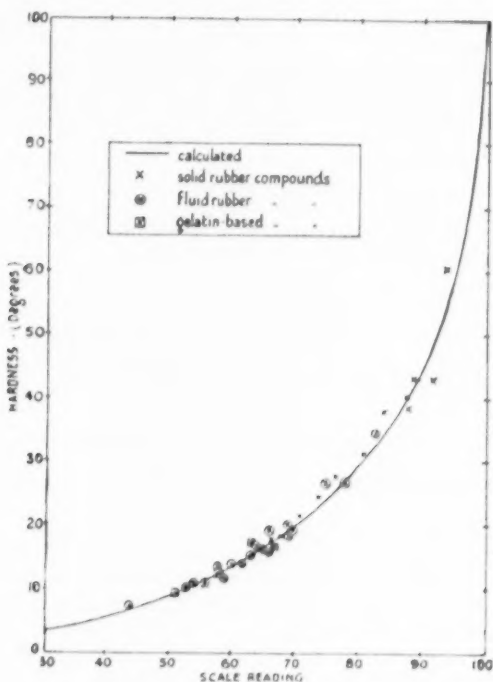


FIG. 2.

The scale is calibrated by the use of a modification of Scott's relationship¹, using appropriate values for load and indenter diameter, the useful range being from 4 to 40 hardness degrees. The hardness readings obtained cannot, of course, be referred to as British Standard Degrees, since the use of a 70-gram load is not covered in a British Standard, but, apart from the name, the new degrees are exactly equivalent to BS degrees above 30, and may be regarded as extending the range downwards for lower values.

For a gauge calibrated in hundredths of a millimeter or in thousandths of an inch, the reading may be converted into hardness degrees by means of Table 1, while for a gauge calibrated in BS degrees, the conversion is given in Table 2; in the latter case it is possible to add a second scale to the gauge.

SOME TYPICAL RESULTS

Figure 2 shows the theoretically calculated curve, together with some points obtained experimentally from a number of compounds based on both solid and fluid rubbers, and also gelatin-based printing roller compositions. It is seen that the agreement is remarkably good up to about 45° BS ("Standard" readings were made, using a 535-gram load and a $\frac{1}{4}$ in. diameter foot).

ACKNOWLEDGMENTS

The writer wishes to thank R. I. Wood (BRPRA), M. Braden (BRPRA) and M. Pike (RTD) for supplying samples, and A. L. Soden (RABRM) for helpful discussions and for the loan of samples of known hardness; also S. S. Hills for the photographs.

The apparatus described forms part of the program of development of physical test methods undertaken by the Board of the British Rubber Producers' Research Association in connection with the program of research which it is carrying out.

REFERENCES

- ¹ Soden, A. L., private communication.
- ² Scott, *J. Rubber Research* 17, 145 (1948); 18, 12 (1949); B.S. 903: 1950, "Methods of Testing Vulcanized Rubber", Part 19.
- ³ Scott, *Trans. Inst. Rubber Ind.* 11, 224 (1935).

OXIDATIVE AND NONOXIDATIVE THERMAL DEGRADATION OF RUBBER *

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The mechanical properties of rubber often undergo a marked change on heating, with deterioration of its elasticity and strength as a result. This behavior is a problem not merely where rubber is used in surroundings of prevailing high temperature; arguments can be advanced to show that thermal deterioration may influence to some extent as seemingly remote a property as wear¹.

The behavior of rubber exposed to heat is strongly influenced by the presence or absence of oxygen. When an ordinary rubber vulcanizate is heated to, say, 100° C in the presence of oxygen or air, it undergoes substantial changes in a comparatively short time. Yet the effects may be similar in the absence of oxygen at temperatures 60° to 100° C higher. The inference is that, although a given rubber heated in air to 100° C, for instance, may be stable owing to its high resistance to oxidation, it may become completely unstable when heated to 180° C on account of thermal decomposition.

This paper is published to provide fuller details of the behavior of rubber when heated in the presence and absence of oxygen. The evidence was obtained from experiments with both unvulcanized and vulcanized rubber, differing in composition.

METHODS OF INVESTIGATION

The following methods were employed to investigate the thermal degradation of rubber.

Oxygen-free heating.—Carius tubes filled with rubber are heated at 90° C for 20 minutes before the experiment proper, constant evacuation to 0.05 mm. of mercury pressure being applied, to exclude oxygen. The tubes are then rinsed three times in succession with nitrogen and are evacuated again, after which they are sealed. From the results of heating tests for long periods at 100° C, which left the rubber virtually unchanged (see, for instance, Figure 8), it was concluded that this procedure also effectively eliminates atmospheric oxygen present in the rubber. Subsequently, these rubber-filled evacuated Carius tubes are heated at a given temperature for a given period in an oil bath.

Estimation of oxygen consumption.—A vast variety of instruments are described in the literature for measuring the amount of oxygen used during the oxidation of rubber². In the one chosen for these experiments the rubber is oxidized in an atmosphere of oxygen at constant pressure; the quantity of oxygen consumed can be determined at any moment by gas volumetry³. Figure 1 gives an over-all diagrammatic illustration of one such apparatus consisting of 12 measuring elements.

In this instrument, the rubber, sealed in a small absorption vessel, A, is kept at constant temperature by means of an electrically heated block of

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aluminum. Each absorption vessel is connected to a gas-measuring system consisting of a calibrated graduated tube, *C*, a parallel tube, *P*, connected with it, and a manual mercury-leveling device, *B*, which makes it possible to take manometer readings at atmospheric pressure.

After repeated evacuation and thorough rinsing, the instrument is filled with oxygen, mercury bulb *B* being turned down and cock *H* closed. Subsequently, tubes *C* and *P* are disconnected by raising bulb *B* at the open cock, *H*, after which tube *P* is connected with the outside atmosphere. By adjusting the mercury reading in tubes *C* and *P* at regular intervals to the same level, oxidation will be made to take place at a nearly constant pressure of 1 atm.

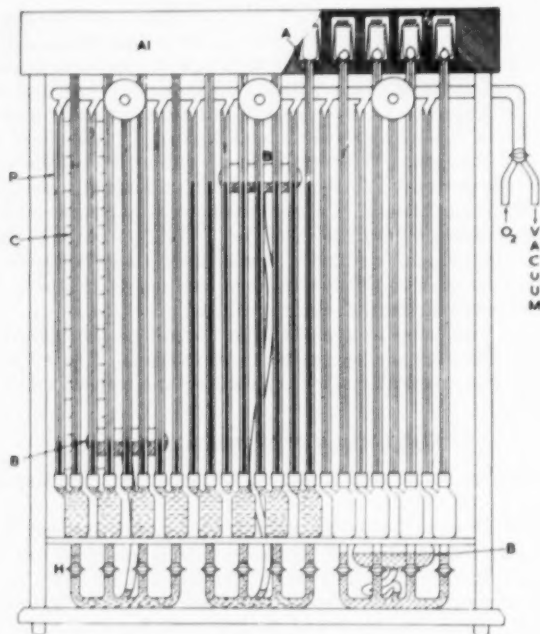


FIG. 1.—Apparatus for measurement of oxygen consumption during oxidation of rubber.

Two of the 12 measuring elements are always left empty to serve as reference against the readings of the other tubes for correction necessitated by variations of outside pressure and temperature. It is generally advisable to have a small amount of soda-lime in the absorption vessels to absorb any carbon dioxide and water formed during oxidation.

The apparatus described can be varied in different ways. The instrument represented in Figure 1, with an absorption vessel of 12-ml. capacity and a gas-measuring tube 70 cm. long with a volume of 0.03 ml. per cm., does very well for 1-gram specimens, or less, of rubber. In one variant the absorption vessel is large enough to contain three dumbbells 3.2×1 mm. in diameter, with which the process of oxidation can be followed after commensurate enlargement of the gas-measuring tube.

The rates of oxidation of rubber are recorded in milliliters of oxygen (at 0° C and 76 cm.) per gram of rubber per hour.

DEGRADATION OF UNVULCANIZED NATURAL RUBBER

The clearest evidence of the effect of degradation on the properties of raw unvulcanized natural rubber is provided by the changes that occur in the mean molecular weight of the rubber molecules. In order to establish this effect, slightly premasticated natural rubber (thin pale crepe No. 1) was heated either in vacuo or in the oxidation apparatus described. The size of each sample for the oxidation measurements was kept below 100 mg., so that the reaction should be as homogeneous as possible.

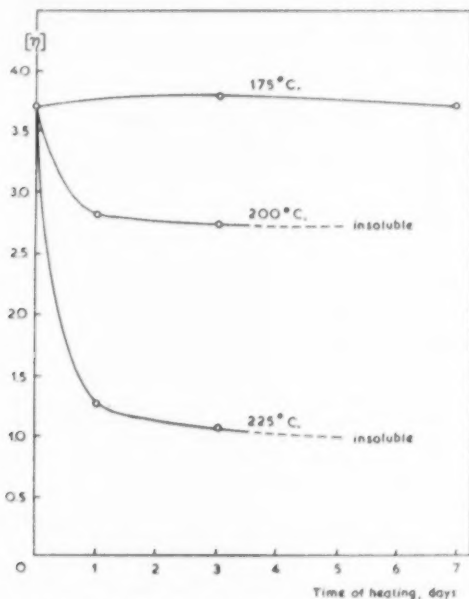


FIG. 2.—Effect of heating in absence of oxygen on intrinsic viscosity of premasticated natural rubber in chloroform.

After the rubber had been heated at the preset time and temperature, it was dissolved in benzene or chloroform and its intrinsic viscosity measured. This intrinsic viscosity is defined as follows:

$$[\eta] = \lim_{C \rightarrow 0} \frac{\eta - \eta_0}{\eta_0 C}$$

where η = viscosity of the solution, η_0 = viscosity of the solvent, and C = concentration in grams per 100 ml. of solution.

Watson⁴ has shown that the intrinsic viscosity is related to the molecular weight, M_n , of the rubber according to the equation $[\eta] = 10^{-5} M_n^{0.98}$. Hence, at a first approximation, $[\eta]$ is proportional to the molecular weight.

Heating without oxygen.—Figure 2 shows that the intrinsic viscosity of slightly premasticated natural rubber in chloroform does not change as the result of heating for 7 days at 175° C. The intrinsic viscosity drops at higher temperatures, but, if the rubber is heated for longer than 3 days at higher temperatures, it becomes partly insoluble, probably as the result of cross-linking. Chloroform was used as a solvent because, in all the cases investigated, hence also after heating at 175° C, the rubber no longer dissolves completely in benzene. This latter phenomenon indicates that a slight change in molecular structure of an unknown nature may have taken place.

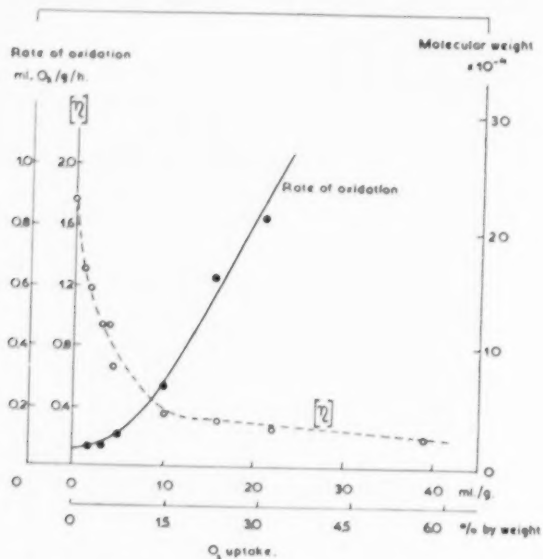


FIG. 3.—Effect of oxygen absorption at 110° C on rate of oxidation and intrinsic viscosity of natural rubber.

The observed changes in the intrinsic viscosity of rubber on heating in the solid state are in some respects similar to the results of Watson⁴ obtained by heating the rubber solutions, themselves, in vacuo. One difference is that changes to be observed in dry rubber on heating to 200° to 225° C begin to occur at 100° to 120° C in rubber solutions.

This decrease of molecular weight on heating might well be explained as the result of a simple thermal chain scission. The detached end fragments of the molecules are apparently capable of entering into cross-linking reactions, in particular in the case of rubber heated in the solid state. Apparently dilution of the system by a solvent slows down this cross-linking reaction to a point where it is dominated completely by the chain-scission reaction.

At temperatures above 250° C, rubber changes very substantially, and a vast number of cracking products of low molecular weight are formed. After 2 hours at 300° C, rubber has degenerated into a viscous, dark-brown oily substance. The higher the temperatures above this, the sooner is rubber converted entirely into oily products, from which substances of very divergent boiling

points can be isolated. The products formed by brief heating at temperatures ranging from 400° to 750° C are conspicuous because they contain a large isoprene fraction, which is generated by direct depolymerization of the polyisoprene molecule. A very short period of heating—of the order of 1 second—and a relatively high cracking temperature strongly promote the formation of isoprene. Under favorable conditions, up to 58 per cent of isoprene can be obtained from raw rubber⁵.

Heating in oxygen.—As will be clear from a comparison of Figure 3 with Figure 2, the heating of raw, slightly premasticated rubber to 110° C in the presence of oxygen leads to a decrease of molecular weight similar to the changes

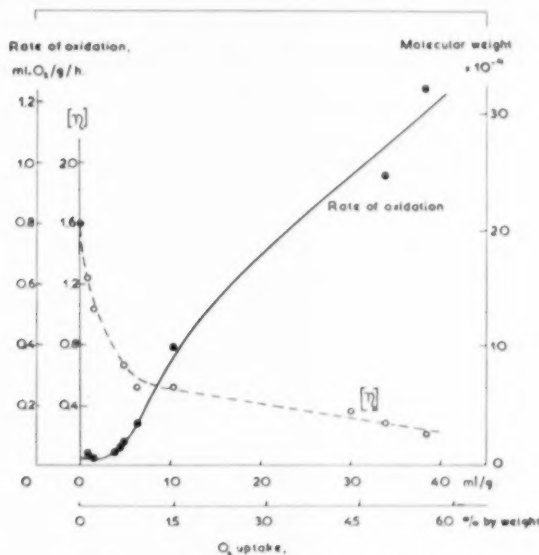


Fig. 4.—Effect of oxygen absorption at 80° C on rate of oxidation and intrinsic viscosity of natural rubber of low protein content.

produced by heating without oxygen. A fundamental difference exists, however, in that the intrinsic viscosity is plotted against the time in Figure 2, whereas in Figure 3 it is plotted against the amount of oxygen absorbed.

It appears that, without oxygen, it is necessary to heat the material to a temperature higher by about 100° C to obtain in roughly the same time approximately the same changes in the rubber as with oxygen, at any rate as far as the initial drop in viscosity is concerned.

It is predominantly the oxygen absorbed at the beginning of the process that causes a very pronounced reduction of the molecular weight of the rubber. After an uptake of 0.7 per cent by weight of oxygen, further absorption reduces the molecular weight to a greatly diminished degree. The bend in the curve coincides with the termination of the induction time of oxidation. Above that point, there is an enormous autocatalytic increase of the rate of oxidation, presumably because the antioxidants originally present in the rubber are used up at this stage. Hence the reaction with oxygen has produced a rubber which is

far more sensitive to oxidation. It looks as if the reaction mechanism of the oxidation of rubber in this autocatalytic range has become different from what it was previously. In this range of rapid oxidation, the rubber apparently combines with a large amount of oxygen without chain scission. Possibly the latter is here compensated for by cross-linking reactions.

The relation between absorption of oxygen and rate of oxidation or intrinsic viscosity was also estimated in crepe of low protein content. Since this rubber oxidizes far more readily than ordinary raw rubber, the experiments were performed at 80° instead of 110° C. The behavior of this type of rubber, as represented in Figure 4, differs little from that of ordinary rubber, as shown in

TABLE I
RATE OF OXIDATION OF VARIOUS TYPES OF RUBBER

	Temperature (° C)				
	80	80	110	110	110
	Range of time (Hours)				
	0-6	6-24	0-3	3-6	6-24
	Ml. O ₂ /Gram/Hour				
Crepe 1	—	0.0006	0.003	0.005	0.04
Smoked sheet (RSS 1)	—	0.002	0.004	0.02	0.05
Blanket crepe 3	—	0.013	0.20	0.16	0.30
Blanket crepe 4	—	0.003	0.024	0.03	0.06
Crepe of low protein content	—	0.003	0.43	0.60	Fast
Crepe, sol fraction	0.055	0.9	—	—	—
Crepe, gel fraction	0.80	3	—	—	—
Sheet, sol fraction	1.5	Fast	—	—	—
Sheet, gel fraction	0.03	0.07	—	—	—
Crepe, acetone- extracted	0.3	Fast	10	—	—
Sheet, acetone- extracted	0.003	0.006	0.08	—	—
GR-S	—	0.05	0.12	—	0.10
Perbunan-18	—	0.007	0.16	—	0.15
Neoprene	—	0.035	0.15	—	0.16
Butyl rubber	—	0.00	0.00	—	0.00

Figure 3. In this case, too, an initial rapid reduction of molecular weight is associated with a comparatively low rate of oxidation. As soon as the rate of oxidation reaches the autocatalytic stage, the molecular weight becomes far less susceptible to the influence of oxygen absorption.

Both Figure 3 and Figure 4 make it plain that it is impossible to express the rate of oxidation of a rubber exactly by a single number; at a given moment, the rate of oxidation depends in very large measure on the quantity of oxygen previously absorbed, or, to put it differently, on the antecedent time of oxidation. Actually, a complete oxygen absorption-time curve would always be needed for the presentation of a satisfactory oxidation characteristic. Since this is often cumbersome, especially when long series of measurements are involved, a single value is given in the ensuing pages for the rate of oxidation, representing either the mean rate of oxidation in the autocatalytic range, or the mean rate of oxidation within an indicated range of oxidation time.

INFLUENCES AFFECTING OXIDIZABILITY OF RUBBER

Different kinds of rubber, whether vulcanized or not, often differ considerably in their reactivity with oxygen. Ultimately, the reactivity of vulcanized rubber is governed by various factors, such as the type of rubber, the presence of antioxidants, vulcanization accelerators, fillers and, finally, the vulcanization reaction itself.

Types of rubber.—As Table I shows, different types of rubber differ conspicuously in their readiness to oxidize. Generally speaking, raw natural rubbers have very little tendency to oxidize. There can be little doubt that this resistance to oxidation is due to the presence of natural antioxidants, a fact which may be inferred from the very much greater oxidizability of crepe of low protein content and, more especially, of crepe extracted with acetone. Strangely enough, acetone extraction has comparatively little effect on the oxidizability of smoked sheet rubber.

TABLE II
INFLUENCE OF VULCANIZATION ACCELERATORS ON RATE OF
OXIDATION OF NATURAL RUBBER (CREPE)

	Temperature (° C)			
	80	80	110	110
	Range of time (Hours)			
	0-5	5-24	0-3	3-6
	ML. O ₂ /Gram/Hour			
Without additive	0.002	0.002	0.04	0.04
1% diphenylguanidine	0.032	—	0.2	→ 5
1% mercaptobenzothiazole	0.07	—	0.3	→ 4
1% benzothiazolyl disulfide	0.004	—	0.2	0.2
1% cyclohexyl-2-benzothiazole sulfenamide	0.003	—	0.2	0.2
1% diphenylguanidine + 3% ZnO	0.09	0.20	0.7	→ 17
1% mercaptobenzothiazole + 3% ZnO	0.004	0.004	0.03	0.06

For purposes of comparison, Table I also includes some particulars relating to synthetic rubbers. GR-S, Neoprene, and Perbunan are all more oxidizable than raw natural rubber, contrary to data published in the literature⁶. Butyl rubber, indubitably, as the result of its saturated character, is particularly resistant to oxidation.

The rates of oxidation of the sol and gel rubber fractions of crepe and smoked sheet isolated from a benzene solution are likewise listed in Table I, from which it appears that sol crepe and gel sheet are comparatively slow to oxidize, whereas gel crepe and sol sheet oxidize very readily. This fact, in conjunction with the result of the effect of acetone extraction on sheet and crepe, implies that the natural antioxidants contained in smoked sheet are not soluble in acetone or benzene, whereas those in crepe are.

Fillers.—It is known from previous investigations that addition of carbon black of small particle size—in particular, channel black—leads to increased oxidizability of the rubber⁷.

Vulcanization accelerators.—Table II clearly shows that the addition of certain vulcanization accelerators to rubber increases the rate of oxidation enormously, diphenylguanidine and mercaptobenzothiazole being particularly

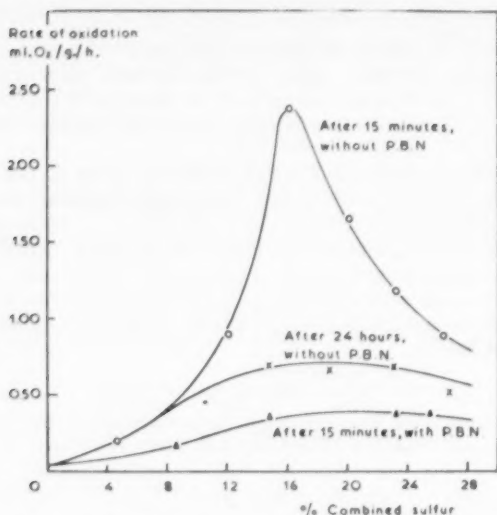


FIG. 5.—Effect of combined sulfur on rate of oxidation of vulcanized natural rubber at 80° C.

potent in this respect. There is an obvious connection between the known peptizing action of mercaptobenzothiazole and this increased rate of oxidation. The inference then is that the action of this mercaptan in the mastication of rubber is induced not only by its power to combine with free radicals⁸, but also by a catalytic effect on oxidation.

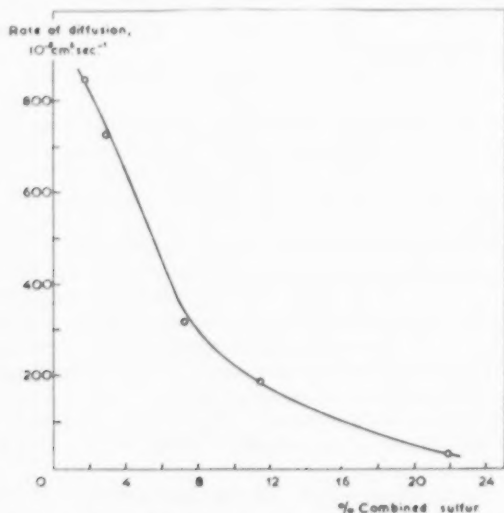


FIG. 6.—Influence of amount of combined sulfur in natural rubber on rate of diffusion of nitrogen gas at 80° C.

That mercaptobenzothiazole does not adversely affect the resistance of rubber vulcanizates to oxidation might be due to the fact that this substance ceases to promote oxidation as soon as zinc oxide is added.

Unlike mercaptobenzothiazole, diphenylguanidine is strengthened in its oxidizing effect by the addition of zinc oxide. The weak resistance of diphenylguanidine vulcanizates to aging is perfectly consistent with this fact.

Vulcanization.—Although some information is available respecting the influence of vulcanization and the associated combination of sulfur on the oxidation rate of rubber³, this influence was again studied, using the author's technique, on the following vulcanizates: (1) natural rubber (RSS 1) 100 parts, sulfur 40 parts, diphenylguanidine 1 part, vulcanized for 5 to 180 minutes at 142° C, and (2) natural rubber (RSS 1) 100 parts, sulfur 1 to 30 parts, diphenylguanidine 1 part, vulcanized for 120 minutes at 147° C.

TABLE III
COMPOSITION OF RUBBER COMPOUNDS

Mix number	A1	A2	A3	A4	A5
Rubber (RSS 1)	100	100	100	100	—
GR-S cold rubber	—	—	—	—	100
Zinc oxide	5	5	5	5	5
Stearic acid	1	1	1	2	2
Sulfur	2	2	—	—	2
Santocure (cyclohexyl-2-benzothiazole sulfenamide)	1	1	—	—	1.6
Tetramethylthiuram disulfide	—	—	3.5	3.5	—
Phenyl-2-naphthylamine	1	1	1.5	1.5	1
Carbon black	—	50	—	—	—
Vulcan 3 (HAF black)	—	—	—	50	50
Time of vulcanization (min.)	30	25	30	20	45
Temperature of vulcanization (° C)	142	142	142	142	142

The following types of carbon black were used in compound A2: Thermax (MT), Sterling 80 (FEF), Vulcan 3 (HAF), Vulcan 9 (SAF), Spheron 9 (EPC), and Spheron 4 (HPC).

The combined sulfur contents of the vulcanizates were determined. Rubbery vulcanizates were cut into 2 × 2 × 2 mm. cubes, whereas the harder, ebonitelike products were filed down to a coarse powder before testing for rate of oxidation.

Just how dependent the oxidation rate of rubber is on the quantity of combined sulfur is evident from Figure 5. The rate of oxidation of a product containing 16 per cent of combined sulfur is 20 to 100 times that of a normal rubber vulcanizate of low combined sulfur content.

There may be two causes for the decreasing rates of oxidation when the percentages of combined sulfur are higher still. One is the slow diffusion of gases in these ebonitelike products, as Figure 6 shows for nitrogen¹⁰. Although these products are pulverized, the limited rate of diffusion of oxygen in these materials may be restrictive on oxidation. With larger fragments of ebonite, the slow diffusion is undoubtedly a determining factor on the rate of oxidation.

Another reason for the slowing down of oxidation associated with a high sulfur content may be that the rate of oxidation of markedly oxidizable rubbers is not constant. After a very high initial rate of oxidation, this decreases until, as Figure 5 shows, it reaches a substantially lower figure at the end of 24 hours. Evidently there are a great many active oxidizable places in the rubber molecules at the beginning which, when saturated, leave a less oxidizable material.

There is reason to believe that, at the beginning of the test, the oxidation rate of the ebonitelike materials was faster than appears from Figure 5, particularly in the first 15 minutes, during which no reliable readings could be taken.

It is likewise clear from Figure 5 that oxidation slows down considerably when antioxidants are added.

The fact that the linking of sulfur acts so potently on the rate of oxidation of rubber may be accounted for in various ways. First of all, any chemical intervention disturbs the stability of the rubber molecule. In this respect the influence of sulfur linkage is the same as that of oxygen combination itself. Then, it is possible that thioether or disulfide groups are formed during the sulfur linkage which may, themselves, easily be oxidized.

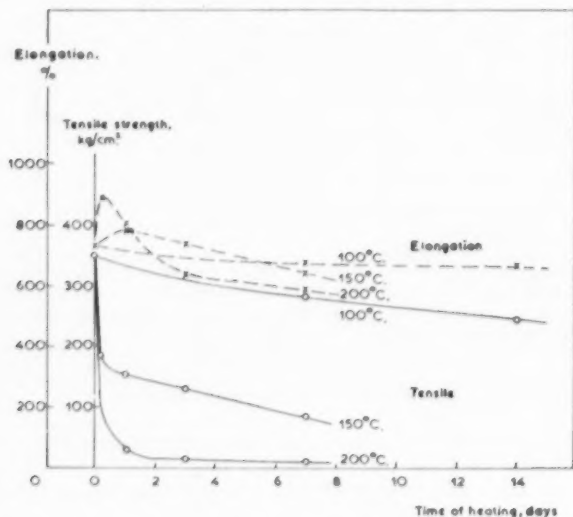


Fig. 7.—Influence of oxygen-free heating on tensile strength and elongation at break of natural rubber pure gum vulcanizate (A1).

The general conclusion to be drawn is that for a high oxidation resistance the least practicable amount of sulfur should be combined in the vulcanization of rubber.

DEGRADATION OF VULCANIZED NATURAL RUBBER

The radical changes which the mechanical properties of vulcanized rubber undergo when it is heated, whether in oxygen or not, have a significant bearing on the practical aspect of the industrial application of rubber. Yet the majority of the experiments carried out relative to these changes have been performed only in the presence of oxygen¹¹.

The procedure used in this investigation was to heat three rubber dumbbells, either in Carius tubes from which oxygen had been evacuated, or in the oxidation measuring apparatus. When the material had been heated for the requisite length of time, certain properties, such as tensile strength, elongation

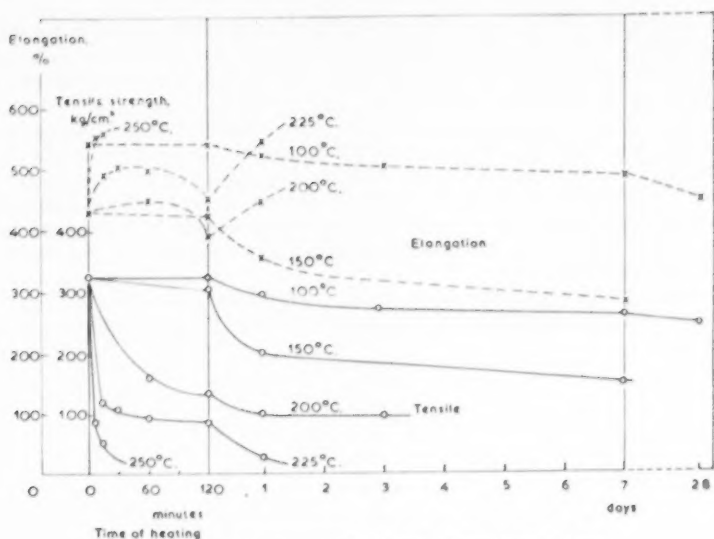


FIG. 8.—Influence of oxygen-free heating on tensile strength and elongation at break of natural rubber-HAF black vulcanizate (A2).

at break, hardness, and swelling, were determined. The rubber compounds used for this purpose are listed in Table III.

Heating without oxygen.—The effect of heating in the absence of oxygen for progressive periods at a temperature of 100°, 150°, or 200° C on a pure gum compound vulcanized with Santocure is to be seen in Figure 7.

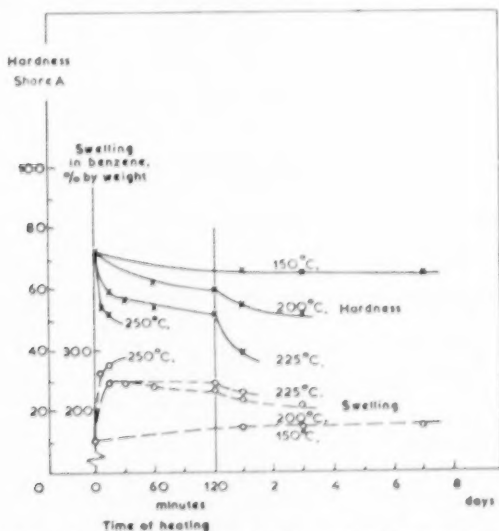


FIG. 9.—Effect of oxygen-free heating on hardness and swelling capacity of natural rubber-HAF black vulcanizate (A2).

Whereas, at 100° C, the tensile strength remains virtually stable for weeks on end, at 150° C it drops to roughly half the value in a few hours. If heating to 150° C is continued, this tensile strength, which had decreased so substantially in the first few hours, remains more or less level. The vulcanized rubber apparently contains a number of unstable bonds which are easily broken down. Once that has happened, the rubber is hardly less stable than raw rubber.

At 200° C the tensile strength declines rapidly, reaching extremely low values. Elongation at break increases somewhat at first, which points to a process of devulcanization. Evidently, direct chain scission, which also takes place in raw rubber, begins to exert a significant influence on the course of events at this temperature.

For many uses to which rubber is put, a pertinent question is the behavior of rubber vulcanizates reinforced with carbon black. Figures 8 and 9 reproduce

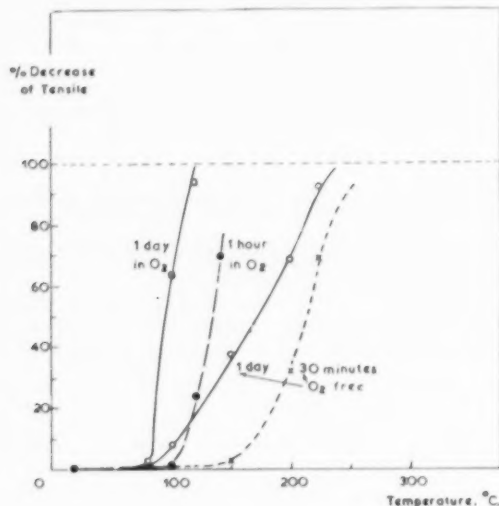


Fig. 10.—Effect of heating on tensile strength of natural rubber-HAF black vulcanizate (A2). At various temperatures in presence or absence of oxygen.

the results obtained with a vulcanizate filled with HAF black. If these figures are compared with Figure 7, it will be seen that the addition of carbon black enhances the thermal stability of rubber considerably. At 100° C the thermal stability of carbon black compounds in the absence of oxygen is particularly satisfactory (see Figure 8). In this case, too, after being heated to 150° C, the rubber remains stable for several days after an initial drop in tensile strength. At 200° C and higher temperatures the drop of tensile strength is precipitous in a very short time. Concomitants of this change in tensile strength are increased swelling capacity and reduced hardness.

The striking dependence of changing mechanical properties on the temperature factor during oxygen-free heating is obvious from both Figures 7 and 8 and is clarified by Figure 10 for the vulcanizate filled with HAF black.

Heating in oxygen.—The behavior of a pure gum and of a HAF black compound on oxidation is illustrated in Figures 11 and 12. In both cases the ab-

sorption of oxygen causes a steep drop of tensile strength. A striking feature is the temperature function of the rate of oxidation and the decline in tensile strength. Figure 13 confirms the fact established by Kemp, Ingmanson, and Mueller¹², that raising the temperature of oxidation has two effects: marked acceleration of oxidation and a greatly accelerated decline of tensile strength after absorption of the same amount, e.g., 1 per cent, of oxygen. Whereas 1 per cent of oxygen can be absorbed at 80° C without undue damage, at 100° C it has a disastrous effect.

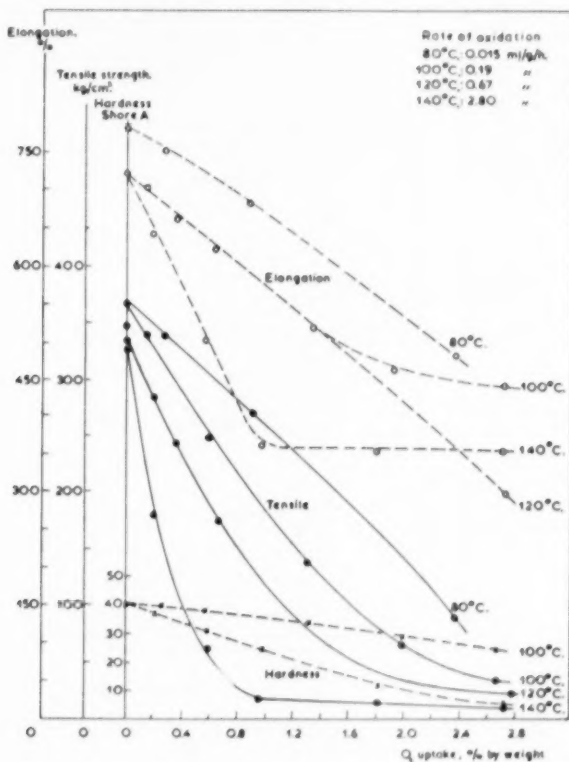


Fig. 11.—Effect of oxygen absorption on tensile strength, elongation at break, and hardness of natural rubber pure gum compound (A1). Oxidation at various temperatures.

Vulcanized rubber heated in oxygen loses strength far sooner and at a much lower temperature than without oxygen. This is clearly brought out in Figure 10, which shows the effect on tensile strength of heating in the presence or absence of oxygen for a stipulated time at various temperatures. To reduce the tensile strength by 50 per cent in one day, for example, the material has to be heated to approximately 170° C without oxygen, whereas with oxygen the same decline in strength occurs at only 95° C. It is also clearly seen how strongly the decline of tensile strength depends on the temperature when oxygen is present.

Plotting the rates of oxidation given in Figure 13 logarithmically against $1/T$, the energy of activation for the oxidation rate can be shown by calculation to be 24.7 kcal. per mole for the pure gum compound and 18 kcal. per mole for the carbon black compound which, in the latter case, is slightly lower than the value recorded by Shelton, Wherley, and Cox¹² as the result of their measurements, this being in both cases 23.6 kcal. per mole.

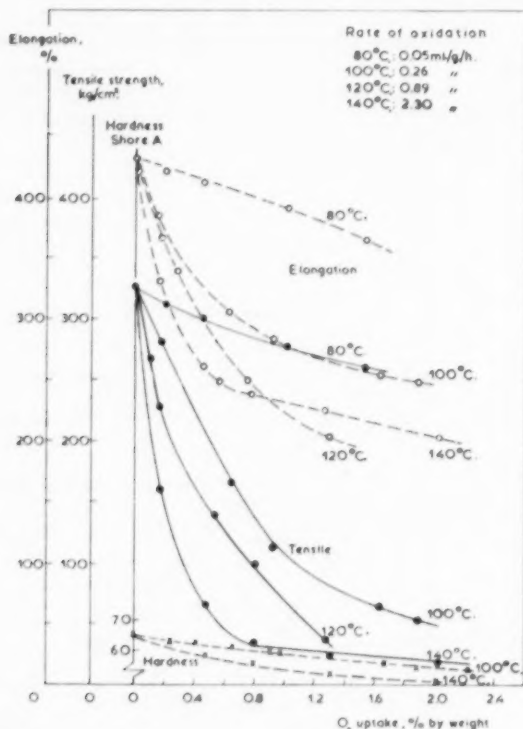


Fig. 12.—Effect of oxygen absorption on tensile strength, elongation at break, and hardness of natural rubber-HAF black vulcanizate (A2). Oxidation at various temperatures.

There would appear to be strong evidence¹³, including that provided by Figures 11 and 12, that oxidation at the higher temperatures has a totally different effect from oxidation at the lower temperatures, notably that accelerated aging at 70° or 100° C is a different process altogether from natural aging at room temperature. The lower the temperature, the larger is the percentage of oxygen that can be combined without serious loss of tensile strength.

Figure 14 shows the influence of a number of carbon blacks on the fall of tensile strength after absorption of oxygen at 100° C; it appears not only that the channel black compounds oxidize faster than the furnace black compounds, but also that in the former case there is considerably greater percentage reduction of tensile strength for a given quantity of oxygen.

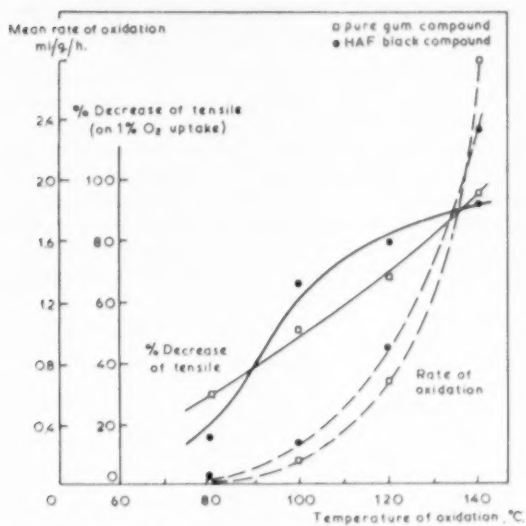


FIG. 13.—Effect of temperature on rate of oxidation and decrease of tensile strength.

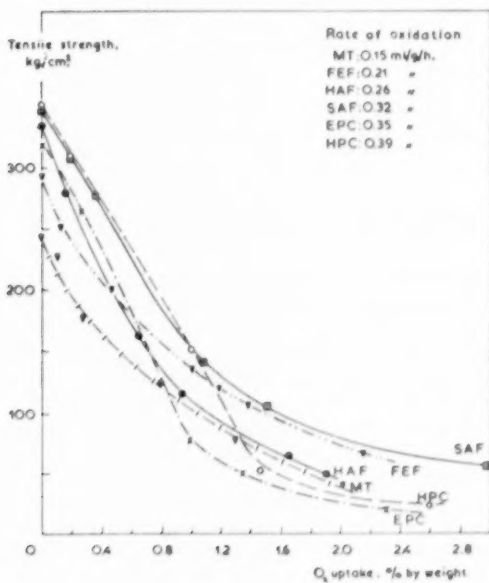


FIG. 14.—Effect of oxygen absorption at 100° C on tensile strength of natural rubber-black vulcanizate (A2). $\frac{1}{2}$

DEGRADATION OF TETRAMETHYLTHIURAM DISULFIDE VULCANIZATES

Tetramethylthiuram disulfide is able to vulcanize natural rubber without the addition of free sulfur. The resulting vulcanizates contain only the small amount of combined sulfur derived from the tetramethylthiuram disulfide itself.

One of the outstanding properties of these tetramethylthiuram disulfide vulcanizates is their great heat resistance¹⁴. Linking of sulfur with rubber particularly accelerates oxidation. The obvious inference is, therefore, that the high heat resistance of these vulcanizates is due to low rate of reaction with oxygen, which, in turn, is due to a very low content of combined sulfur. That this line of reasoning is correct is borne out by the results of heating experiments.

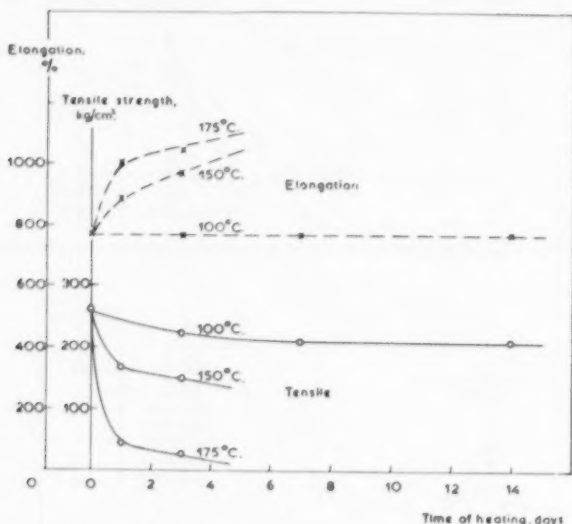


FIG. 15.—Influence of oxygen-free heating on tensile strength and elongation at break. Natural rubber pure gum compound (A3) vulcanized with tetramethylthiuram disulfide.

Heating without oxygen.—Figure 15, representing the behavior of a natural rubber pure gum compound, vulcanized with tetramethylthiuram disulfide, shows that the changes of tensile strength are similar to those occurring in a normal sulfur-Santocure vulcanizate (compare Figure 7). The very marked increase of elongation at break, however, is indicative of very considerable devulcanization or reversion. There is also an increased swelling tendency, viz., after heating for 3 days at 150° C, the swelling in benzene is increased from 380 to 520 per cent by weight, whereas the swelling of a normal Santocure vulcanizate is still unchanged.

This greater devulcanizing tendency can be explained by the fact that these tetramethylthiuram disulfide vulcanizates contain comparatively few cross-links; there is, moreover, no sulfur present to form new cross-links. Therefore, if any links are broken down, a seemingly unvulcanized rubber results, having little tensile strength, pronounced extensibility, and marked flow.

The results obtained with a nonsulfurous HAF black-tetramethylthiuram

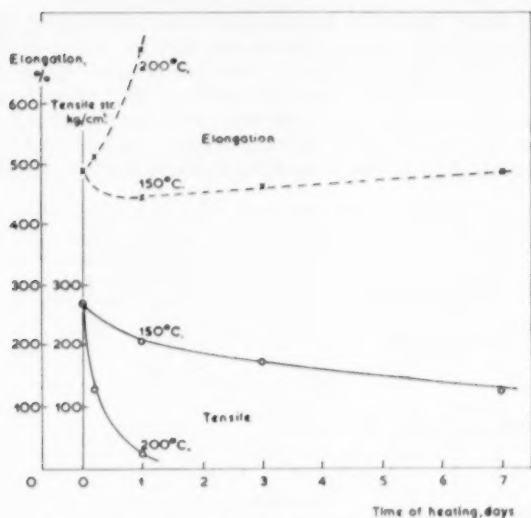


Fig. 16.—Influence of oxygen-free heating on tensile strength and elongation at break. Natural rubber-HAF black compound (A4) vulcanized with tetramethylthiuram disulfide.

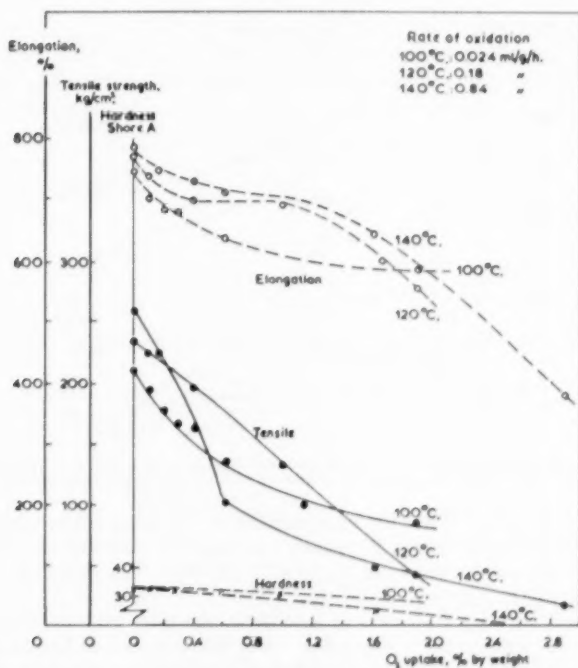


Fig. 17.—Effect of oxygen absorption on tensile strength, elongation at break, and hardness. Natural rubber pure gum compound (A3) vulcanized with tetramethylthiuram disulfide.

disulfide vulcanizate reputedly heat-resistant are reproduced in Figure 16. Such differences as can be detected compared with the behavior of the normal Santocure-black vulcanizate in Figure 8 are not in favor of the tetramethylthiuram disulfide vulcanizate. Predominantly at 200° C its tensile strength deteriorates far more rapidly than does that of the Santocure vulcanizate.

The conclusion is that, in the absence of oxygen, it is inadvisable to use tetramethylthiuram disulfide vulcanizates when thermal stability is required.

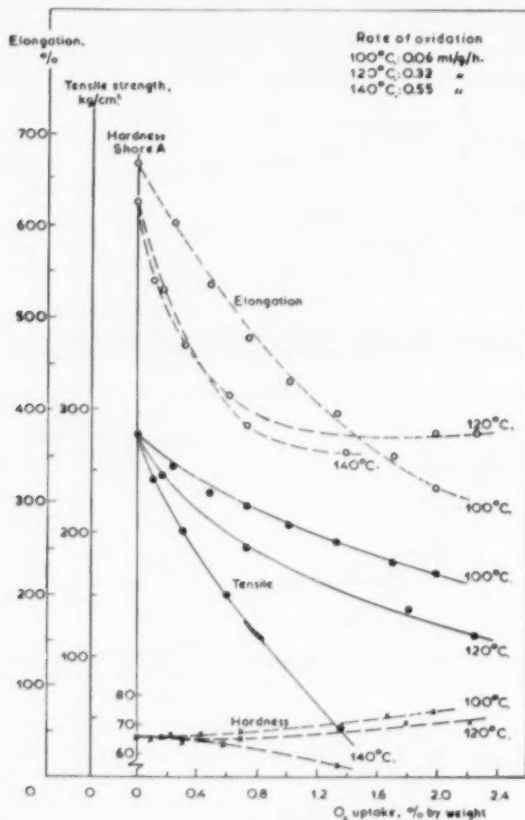


Fig. 18.—Effect of oxygen absorption on tensile strength, elongation at break, and hardness. Natural rubber-HAF black compound (A4) vulcanized with tetramethylthiuram disulfide.

Heating in oxygen.—That the heat resistance of natural rubber-tetramethylthiuram disulfide vulcanizates is, in fact, the result of resistance to oxidation is borne out by the results shown in Figures 17 and 18, which should be compared with those given in Figures 11 and 12.

Apart from its very slow rate of oxidation, the pure gum compound is not conspicuous for satisfactory properties. But the natural rubber-carbon black compound vulcanized with tetramethylthiuram disulfide combines outstanding resistance to oxidation with good mechanical properties. For example, after

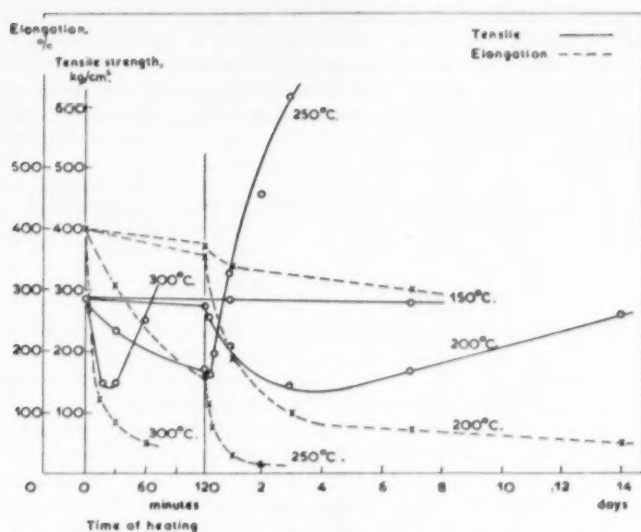


Fig. 19.—Influence of oxygen-free heating on tensile strength and elongation at break. GR-S cold rubber-HAF black vulcanizate (A5).

the absorption of 1 per cent of oxygen at 100° C, the decline in tensile strength is only 16 per cent as against 69 per cent in the case of the similar Santocure compound. Moreover, the rate of oxidation of the former is only 27 per cent of that of the latter.

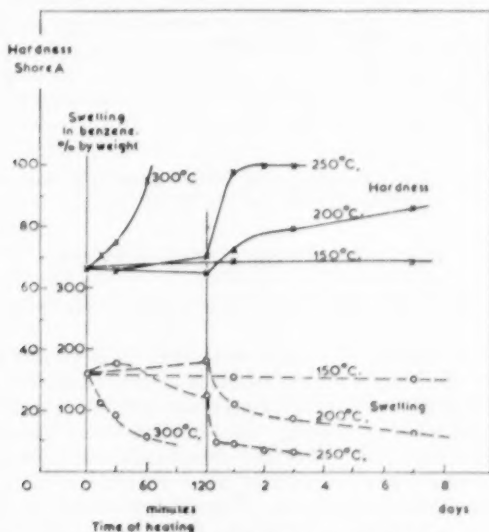


Fig. 20.—Effect of oxygen-free heating on hardness and swelling capacity. GR-S cold rubber-HAF black vulcanizate (A5).

This provides another illustration of the fact that not only is a slow rate of oxidation intrinsically beneficial, but, in addition, it causes a form of rubber-oxygen linkage which is less detrimental to the tensile strength.

The hardness of the carbon black compound increases slightly on oxidation in the range of 80° to 120° C, contrary to that of the other rubber compound, which generally decreases.

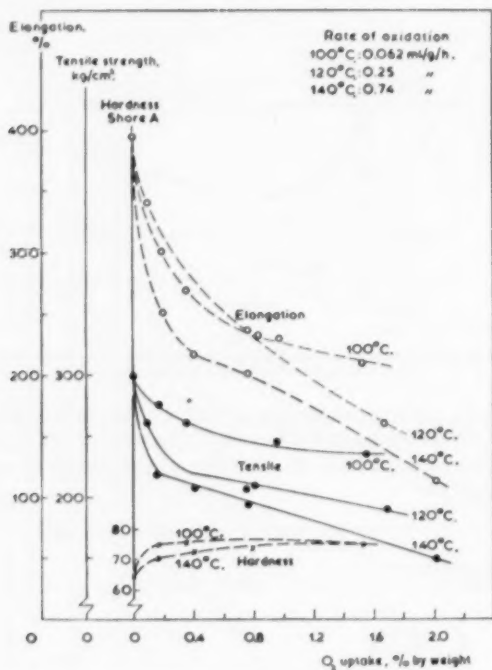


FIG. 21.—Effect of oxygen absorption on tensile strength, elongation at break, and hardness. GR-S cold rubber-HAF black vulcanizate (A5).

BEHAVIOR OF GR-S COLD RUBBER

In some respects GR-S cold rubber behaves differently from natural rubber when heated.

Heating without oxygen.—Figures 19 and 20 show how some properties of a GR-S cold rubber-HAF black vulcanizate change when heated without oxygen.

Whereas (see Figures 8 and 9) the tensile strength of natural rubber steadily deteriorates as the result of heating, accompanied by an over-all weakening, the tensile strength of GR-S cold rubber eventually increases again to a high figure, in conjunction with which there are a general hardening and marked impairment of the elongation at break. The difference between the two rubbers can be accounted for by assuming that the dominant reactions during heating are chain scission in natural rubber and thermal cross-linking in GR-S cold

rubber. The latter also accounts for the greatly reduced swelling capacity of the GR-S after heating.

Heating in oxygen.—Figure 21 represents the behavior during oxidation of a GR-S cold rubber vulcanizate filled with HAF black. Comparing this figure with Figure 12, it will be seen that for the same amount of absorbed oxygen the tensile strength of the GR-S cold rubber compound has decreased far less than in the analogous case for natural rubber¹⁵. Oxidation is also slower. The oxidation of GR-S cold rubber, however, involves appreciable loss of elongation at break and increased hardening; so apparently a good deal of cross-linking takes place.

DISCUSSION AND CONCLUSIONS

The evidence shows that the changes in properties which take place when rubber is heated may be both purely thermal and oxidative. The heating of unvulcanized natural rubber, in either the presence or absence of oxygen, depresses the intrinsic viscosity. One of the changes in vulcanized rubber is loss of tensile strength. The presence of oxygen is noticeable principally in the accelerated rates of reaction with which these changes take place. At temperatures as low as 80° to 140° C, the oxidative degradation reaches a rate of reaction of the same order as that of the purely thermal degradation in the absence of oxygen at temperatures higher by 60° to 100° C.

A characteristic difference between the behavior of natural rubber and of GR-S is that thermal breakdown reactions predominate in the former, both under purely thermal and oxidative conditions, whereas in both conditions cross-linking reactions take place in GR-S.

A heat-resistant vulcanized rubber should have a low reactivity with oxygen. In this respect GR-S compares favorably with natural rubber. However, natural rubber vulcanized with tetramethylthiuram disulfide affords proof that satisfactory results can also be obtained with natural rubber.

It is not only the quantity of oxygen which is responsible for the deterioration of the material's properties, but also the rate of oxidation. Higher rates of oxidation are associated with greater loss of strength after the absorption of a certain quantity of oxygen. This fact is clearly established by the behavior of the rubber in response to the temperature; from this and from older investigations¹⁶ it is to be seen that both the deterioration in strength for a given absorption of oxygen and the rate of oxidation increase with increasing temperature.

The satisfactory heat resistance of natural rubber-tetramethylthiuram disulfide-black vulcanizates is compatible with this picture. Compared with normal vulcanizates, there is not only a very slow rate of oxidation, but also far less deterioration of strength for a given absorption of oxygen. In the absence of oxygen, this vulcanizate is not to be preferred above a normal Santocure vulcanizate as far as thermal stability is concerned.

This dependence of decreasing strength on the rate of oxidation may seriously upset an assessment of the aging behavior of rubber on the basis of accelerated aging tests made at 70° or 100° C, as Shelton, Wherley, and Cox¹³ have observed. It is true that the deterioration of strength to be observed after the absorption of a given quantity of oxygen at, say, 70° C, is by no means comparable to that which takes place at room temperature on absorption of the same amount of oxygen. It would be necessary to measure oxidation rates and deterioration

rates at various temperatures before the "oxidation behavior" of rubber could legitimately be extrapolated to room temperature.

THERMAL STABILITY AND WEAR

The resistance to abrasion of GR-S cold rubber tire treads at ambient temperatures above approximately 13° C is known to be better than that of natural rubber¹⁷. This is difficult to explain on the ground of pure mechanics. If the mechanical properties of natural rubber are compared with those of GR-S, they are found to be either on a par or in some respects better for natural rubber. For instance, the tear strength of a natural-rubber tread compound is three times that of a GR-S tread compound.

To explain the different wear behavior of the two types of rubber, it is probably necessary to take into consideration not only the mechanical-physical properties, but also the chemical properties of the rubber.

It is very easy to establish that, under certain conditions, temperature of a running motor-car tire may rise to 60° to 100° C, mainly on account of hysteresis energy losses. A considerably higher rise in temperature, e.g., up to 200° to 300° C, could, however, occur on a molecular scale at critical hot spots of the tire surface, owing to heat of friction generated during cornering or braking. Since this heat quickly dissipates in the bulk of the rubber of the tire, the temperatures mentioned can be present for only a very short time, depending on the heat conductivity of the rubber. This heat may, nevertheless, conceivably influence abrasion to a considerable extent.

From this investigation it appears that natural rubber is thermally decomposed at temperatures of about 200° C, with softening and almost complete loss of strength as the result. The presence of oxygen substantially accelerates this decline of strength, which then becomes apparent at far lower temperatures. In any case, even temperatures of about 100° C will weaken the rubber in the long run on account of oxidative degradation.

Obviously, loss of strength of the rubber tends to accelerate abrasion. The better tread wear resistance of GR-S cold rubber under certain conditions (ambient temperature above 13° C) compared to natural rubber might very well be explained by its greater resistance to heat. As this investigation has shown, a natural-rubber vulcanizate softens on heating at between 150° and 200° C, whereas GR-S cold rubber hardens, while partly retaining its strength.

For all that, even if we admit that wear is to some extent subject to chemical influences, the mechanical properties of rubber are primary. This can be demonstrated by a comparison of, say, GR-S cold rubber with standard (hot) GR-S. Both rubbers have approximately the same thermal resistance, but the mechanical properties and the corresponding wear resistance of standard GR-S are inferior to those of GR-S cold rubber.

ACKNOWLEDGMENT

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REFERENCES

- 1 Amerongen, van, *Kautschuk u. Gummi* **7**, WT-91 (1954); Powell and Gough, *Proc. Third Rubber Technol. Conf.*, London, 1954, p. 460; *Rubber World* **132**, 201 (1955); *RUBBER CHEM. & TECHNOL.* **29**, 187 (1956).

- ² Kohman, *J. Phys. Chem.* **33**, 226 (1929); Milligan and Shaw, *Proc. Rubber Technol. Conf.*, London, 1938, p. 537; Dufraisse, *RUBBER CHEM. & TECHNOL.* **11**, 268 (1938); Shelton and Winn, *Ind. Eng. Chem.*, **38**, 71 (1946); Amerongen, van, *Rev. gen. caoutchouc* **20**, 136 (1943); Carpenter, *Ind. Eng. Chem.*, **39**, 187 (1947); Pollack, McElwain, and Wagner, *Ind. Eng. Chem.* **41**, 2280 (1949); Shelton, "Symposium on Aging of Rubber", Am. Soc. Testing Materials, *Tech. Pub.* **80**, 12 (1949); Baxter, Morgan, and Roebuck, *Ind. Eng. Chem.* **43**, 446 (1951); Blum, Shelton, and Winn, *Ind. Eng. Chem.* **43**, 464 (1951); Pedersen, *Acta Scand.* **4**, 487 (1950); *RUBBER CHEM. & TECHNOL.* **24**, 18 (1951); Pollack, *India Rubber World* **130**, 53 (1954).
- ³ Amerongen, van, *Rev. gen. caoutchouc* **20**, 136 (1943); *RUBBER CHEM. & TECHNOL.* **19**, 170 (1946).
- ⁴ Watson, *Trans. Inst. Rubber Ind.* **29**, 202 (1953).
- ⁵ Boonstra and Amerongen, van, *Ind. Eng. Chem.* **41**, 161 (1949).
- ⁶ Mesrobian and Tobolsky, *J. Polymer Sci.* **2**, 463 (1947).
- ⁷ Shelton and Turnbull, *Ind. Eng. Chem.* **38**, 1052 (1946); Amerongen, van, *Ind. Eng. Chem.* **45**, 377 (1953).
- ⁸ Watson, *Trans. Inst. Rubber Ind.* **29**, 32 (1953).
- ⁹ Dufraisse, and Etienne, *RUBBER CHEM. & TECHNOL.* **11**, 282 (1938).
- ¹⁰ Barrer, and Skirrow *J. Polymer Sci.* **3**, 549 (1948).
- ¹¹ Ingmanson and Kemp, *Ind. Eng. Chem.* **30**, 1168 (1938); Kemp, Ingmanson, and Mueller, *Ind. Eng. Chem.* **31**, 1472 (1939); Winn, Shelton, and Turnbull, *Ind. Eng. Chem.* **38**, 1052 (1946); Shelton and Cox, *Ind. Eng. Chem.* **43**, 456 (1951); **45**, 392 (1953).
- ¹² Kemp, Ingmanson, and Mueller, *Ind. Eng. Chem.* **31**, 1472 (1939).
- ¹³ Shelton, Wherley, and Cox, *Ind. Eng. Chem.* **45**, 2080 (1953).
- ¹⁴ *Vanderbilt News* **1**, 4 (June-July 1931).
- ¹⁵ Shelton and Cox, *Ind. Eng. Chem.* **45**, 392 (1953).
- ¹⁶ Kemp, Ingmanson, and Mueller, *Ind. Eng. Chem.* **31**, 1472 (1939); Shelton, Wherley, and Cox, *Ind. Eng. Chem.* **45**, 2080 (1953).
- ¹⁷ Decker, de, Houwink, and Amerongen, van, *Proc. Third Rubber Technol. Conf.*, London, 1954, p. 749.

THE VISCOSITY AND STRUCTURE VISCOSITY OF RUBBER SOLUTIONS AND EMULSIONS *

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It is well known that the increase of viscosity of a colloidal solution over that of the pure solvent is produced by the frictional resistance to flow of the dispersed particles. The amount of this viscosity increase depends to a great extent on the shape of the particles. If these are spheres, only the ratio of the volume of the solute to the solvent is involved (Einstein's law), while in the other extreme case, namely with fiber molecules, the particle size plays such an important role, as is known, that one can calculate the particle weight of the dispersed phase from the viscosity (Staudinger's law, Mark-Houwink equation). But not only is the viscosity of a colloidal solution influenced by the particle form, but also its structural viscosity depends on it to a great degree. It is easy to understand this. For if the structure viscosity and, consequently, the decrease of viscosity with increasing velocity gradient, result from the fact that the hydrodynamic forces in the flowing solution, on the one hand, orient and distort the dispersed particles in the moving stream, and, on the other hand, oppose an eventual intermolecular mutual effect or aggregate formation of the particles, it is easily seen that the flow forces will be able to manifest these effects all the more readily and markedly the more extended and the stiffer the dispersed particles are. Thus it can be expected that, in general, in spherical particle suspensions no structural viscosity will appear, but that this will manifest itself the more strongly the more asymmetric the particles.

With rubber it is easily possible to realize two extremely different dispersion forms. Rubber emulsions, as they exist in the various latexes, are typical definite spherical suspensions, with rather large particles of very uniform size. In rubber solutions, on the other hand, say in toluene or benzene, there is a macromolecular distribution. The dispersed particles are the individual kinky fiber molecules of the rubber, which are known to have a more or less elongated form. In fact these two types of rubber dispersions behave so differently that each of them can be called a typical representative of its class.

EXPERIMENTAL

Natural-rubber latex was available as a 60 per cent emulsion. Its flow curve was obtained in the Umstaetter structural viscometer. Then, after dilution with water, the specific viscosities at low concentration were measured in the Ubbelodhe viscometer in order to determine the limiting viscosity $[\eta]$. A microscopic examination of the latex showed extremely uniformly large round particles with a diameter of about 0.05 mm. Next the natural rubber was coagulated out of the latex by addition of ethanol, carefully dried, and dissolved

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in benzene or toluene. Then the flow curves were taken again in the Umstaetter structural viscometer, and, in addition, the limiting viscosities in toluene and in benzene were determined. The Hagenbach-Couette correction for the measurements in the Ubbelodthe was calculated by the equation of Schulz⁴. This was neglected for the structure viscosity measurements, since it became insignificant with the chosen apparatus dimensions. The temperature of measurement was always 20° C. The concentrations, unless otherwise stated, are in g. per 100 ml.

RESULTS AND DISCUSSION

NATURAL LATEX (SPHERICAL SUSPENSION)

It has already been shown by Staudinger³ that for latexes the Einstein equation holds:

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = 2.5\phi$$

where η = viscosity of the solution.

η_0 = viscosity of the solvent.

η_{sp} = specific viscosity.

ϕ = concentration by volume.

If one converts this relation ϕ (ml./ml.) to c (g./100 ml.), one obtains (since $c = 100\rho\phi$, where ρ is the density of the solute):

$$\frac{\eta_{sp}}{c} \cdot \rho = 0.025$$

The expression $\frac{\eta_{sp}}{c} \cdot \rho$ is therefore a constant; in particular it is independent of the concentration. Since, however, $\frac{\eta_{sp}}{c}$ for $c \rightarrow 0$ becomes identical with the limiting value of the viscosity $[\eta]$, the further relation holds:

$$[\eta] \cdot \rho = 0.025$$

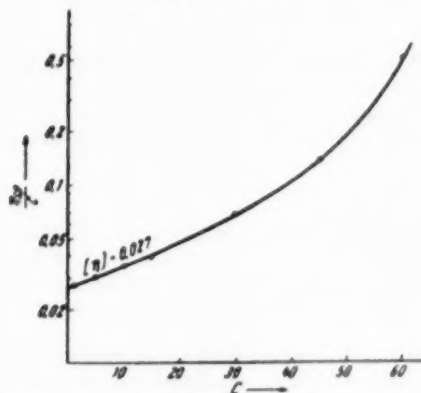


Fig. 1.— η_{sp}/c as a function of c and extrapolation toward $c \rightarrow 0$ for a natural-rubber latex emulsion.

From this it also follows that the product of the limiting viscosity value and the density should be a constant and independent of the concentration. Now since, however, the Einstein calculations are based essentially on the premise that the spherical particles in unit volume of the system are dissolved in such a weak concentration that the existence of a neighboring particle exerts no influence on the motion of the liquid surrounding each individual particle, it is not to be expected that the theoretical value of 0.025 for $[\eta] \cdot \rho$ will hold also for higher concentrations. Nevertheless, as we go to lower concentrations it should be approached, and by extrapolation to zero concentration it should be reached exactly. As Figure 1 shows, this is, in fact, the case. Extrapolation to zero concentration gives $[\eta] = 0.027$. This times the density of rubber $\rho = 0.914$ gives 0.0247, in excellent agreement with the value calculated by Einstein.

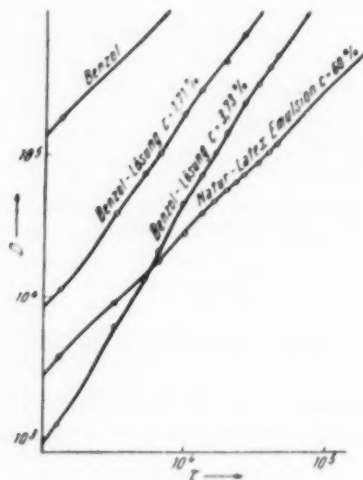


FIG. 2.—Flow curves of natural rubber in benzene solution and as an emulsion (pure benzene for comparison)

Figure 2 shows the measured flow curves, plotted in the usual manner as $\log D$ vs. $\log \tau$ where:

$$D = 4 \frac{Q}{3\pi r^3} \text{ (in sec.}^{-1}\text{)} \quad \tau = \frac{rp}{2l} \text{ (in dynes per cm.}^2\text{)}$$

- Q = volume flowing per second.
- r = radius of the capillary.
- l = length of the capillary.
- p = driving pressure.
- D = average velocity gradient.
- τ = maximum shearing stress.

As the flow curve of natural rubber latex ($c = 60\%$) in Figure 2 shows, this behaves throughout like a Newtonian liquid. Pure benzene is shown as a comparison material. Structure viscosity does not in general appear. This is in the best accord with what is expected from the theory (see above) that sus-

pensions of exactly spherical particles should show no structure viscosity. Finally it is also remarkable that, in spite of the high concentration of 60 per cent, the viscosity increase of the rubber emulsion is relatively slight.

NATURAL RUBBER IN MOLECULAR SOLUTION (FIBER MOLECULES)

Solutions of rubber in toluene or benzene are typical representatives of fiber molecules in solution. It is thus possible, from measurements at low concentrations, to extrapolate to the limiting viscosity value, as is shown in Figure 3. Since the flow gradient in the viscometers used was always less than 500 sec^{-1} , extrapolation to $D \rightarrow 0$ was aimed at. The limiting viscosity values came out

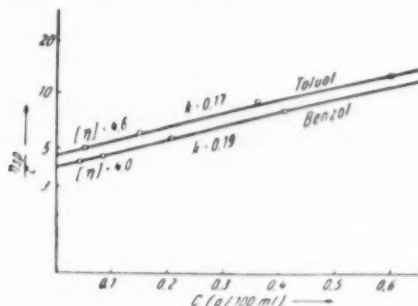


Fig. 3.—Determination of $[\eta]$ for natural rubber, dissolved in toluene and in benzene.

4.6 in toluene and 4.0 in benzene. From the slope of the straight lines in Figure 3 one can calculate the first mutual effect constant k of the extrapolation equation used:

$$\log \frac{\eta_{sp}}{c} = \log[\eta] - k[\eta]c \quad (\text{Martin's equation})$$

This gives $k = 0.17$ for toluene and $k = 0.19$ for benzene. This indicates that toluene must be considered the better solvent. From these k values which correspond to the Martin equation, one obtains those which belong to the Huggins equation by multiplying by 2.3. From the limiting viscosity value, the molecular weight is calculated by the equation:

$$[\eta] = KM^\alpha$$

For toluene the values $K = 5 \times 10^{-3}$ and $\alpha = 0.67$ are known³, and from these a molecular weight of 830,000 is obtained. For benzene we were unable to find the values for the constants K and α anywhere. With the plausible assumption that α has the same value as for toluene we get for benzene a K value of 4.4×10^{-3} .

In this connection it should be pointed out that the attempts to standardize data with regard to limiting viscosity value and the concentration have led to the unfortunate result that, at the present time, there are three different possible ways of stating them, which are all employed, corresponding to the three

concentration units: in g. per l., g. per 100 ml., and g. per ml. The corresponding limiting viscosity figures are related as follows:

$$Z\eta = [\eta](c \text{ in g./l.}) = \frac{1}{10} [\eta](c \text{ in g./100 ml.}) = \frac{1}{1000} [\eta](c \text{ in g./ml.})$$

In Figure 2 there are also shown the flow curves of two rubber solutions with benzene. It may be noted that these solutions, unlike an emulsion, show very pronounced structure viscosity, a fact that has already been known since the measurements of Philippoff. The flow curves have the typical S shape and make possible an estimate of η_{∞} (limiting value of the viscosity for very high velocity gradients). The limiting value η_0 for very low velocity gradients is customarily determined from measurements of the viscosity made by the falling ball method, since, in this method, shearing stresses of about 10 to 100 dynes per sq. cm. are realized.

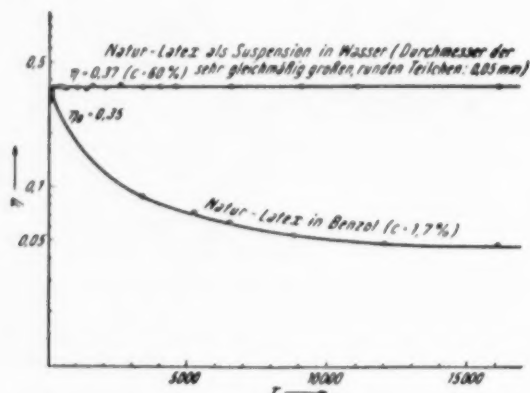


Fig. 4.—Viscosity and structure viscosity of natural rubber as a suspension and as a solution. The legend on the descending curve is: Natural latex in benzene ($c = 1.7\%$). The legend on the horizontal line is: Natural latex as a suspension in water (diameter of the uniformly large spherical particles 0.05 mm.).

In order to bring out the difference in the structure-viscosity behavior of emulsions and solutions more clearly, we have in Figure 4 once more plotted the logarithm of η against τ for both systems. The emulsion gives a horizontal line, that is, its viscosity is constant, whereas that of the solution drops sharply when the shearing stress becomes larger. It is readily seen from this representation that a 60 per cent emulsion and a 1.7 per cent molecular solution have about the same viscosity. Thus for the uniform spheres of the emulsion to produce the same viscosity as the extended molecules of the solution, the material distributed among the spheres must be present in a concentration 35 times as high.

REPRESENTATION AND INTERPRETATION OF STRUCTURE VISCOSITY ACCORDING TO UMSTAETTER

Finally we shall discuss the flow behavior of rubber from the standpoint of the Umstaetter structure mechanics⁴.

Hitherto the problem of the mechanism of structure viscosity has been attacked from two essentially different directions. On the one hand, one considered the individual molecules and sought to calculate their hydrodynamic

behavior as a function of the flow forces and also of the molecular configuration and characteristics and then to integrate over the whole system. This is the molecular method of consideration. On the other hand, one treated the solution as a continuous phase and sought to calculate the laws of flow of this continuous phase according to the classic hydrodynamical methods. This is the continuous method of consideration. In his structure mechanics, Umstaetter has now attempted to combine both methods. He calculates with the customary methods of continuum mechanics but, at the same time, makes the additional assumption that the substrate has a structure, and therefore is not to be divided into arbitrarily small differentials, but only into very small but nevertheless finite differences. As soon as the dimensions of the dissolved substance are involved, one can no longer calculate with differential quotients (derivatives), but only with difference quotients. The magnitude of these "differences" or "extremal values" (according to Umstaetter) of the dimensions of the substance gives us the outer measure of the particles present, and therefore the micelle weight or the molecular weight. Without going further into the mathematical reasoning, it should nevertheless be mentioned that Umstaetter conceives the flow curve as a sort of resonance curve. His argument runs as follows: In the sense of the "position change theory" (Platzwechseltheorie), there can be assigned to each value of the velocity gradient a characteristic position change frequency, namely, the number of particles which it causes to pass by one another per unit time. If now this position change frequency matches the proper frequency (Eigenfrequenz) of the particles, then the change of position takes place especially readily; a "resonance" ensues, the change of viscosity for a given change of velocity gradient is especially great, and the slope of the flow curve attains maximum steepness. This point, however, is the point of inflection of the flow curve. Here the steepness, the "slipperiness" σ is maximal. σ is given as:

$$\sigma = \frac{d \log D}{d \log \tau} = \frac{\tau dD}{D d\tau}$$

If one now defines further a "total viscosity" $\eta = \frac{\tau}{D}$ and a "differential viscosity" $\eta' = \frac{d\tau}{dD}$, there is the further relation:

$$\sigma = \frac{\eta}{\eta'}$$

This means that, when σ reaches a maximum, the differential viscosity is a minimum. If σ is plotted as a function of D , one obtains a sort of "resonance" curve.

Now since the proper frequency of the dissolved particles, for example that of the tangle of molecules, depends on their dimensions, Umstaetter sees here a possibility of an absolute viscometric molecular weight determination. The molecular weight is calculated direct from the "critical velocity gradient" \hat{D} , in which σ is maximal, that is, the flow curve has its inflection point. This calculation is, to be sure, a very complicated one, involving the viscosity-temperature function. In fact the measurements of Umstaetter, Edelmann, and also the author's own measurements, show that for different concentrations of a solution \hat{D} turns out to be a constant, and that it gets smaller and smaller the greater the molecular weight of the dissolved particles. To our knowledge,

however, absolute molecular weight determinations by this method have been carried out only in isolated cases.

Quite apart from these theoretical considerations, however, from the practical standpoint the fact seems highly important that Umstaetter has shown a way of representing in the form of a single straight line the flow curves for different concentrations of a system. To accomplish this, he proceeds from the fact that, according to his calculations, the structure viscosity curve is described by a gamma function. From the function theory, however, it is known that the incomplete gamma function $\Gamma(x, y)$ for $\Gamma(\frac{1}{2}, y^2)$ is identical with the Gauss error function. He proposes, therefore, to plot the expression:

$$\frac{\log (\eta / \eta_{\infty})}{\log (\eta_0 / \eta_{\infty})}$$

vs. $\log D$ in a cumulative probability net (Summenwahrscheinlichkeitsnetz). In this way one is supposed to get straight lines over a range of 6 decades (powers of 10), which contain the measured points of all the concentrations of a

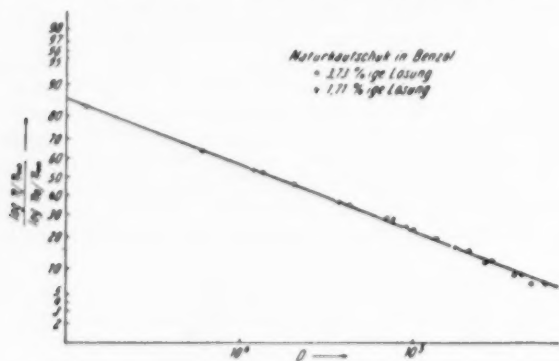


FIG. 5.—Representation of the flow curves of Figure 2 for rubber solutions, according to Umstaetter. The legend on the diagram is: Natural rubber in benzene. ○ 3.73% solution. + 1.71% solution.

system. The inflection point of the flow curve, the value \hat{D} in this representation, lies at 50 per cent in the ordinate. Umstaetter and Edelmann have shown for a series of systems that the above method does actually give straight lines. In particular, it turns out that the slope of these straight lines is independent of the molecular weight. The molecular weight shows up only in the position of \hat{D} , and therefore can probably be considered as a direct measure of the polymolecularity of the sample. In what follows we propose to apply these lines of reasoning of Umstaetter to our measurements of rubber solutions.

In Figure 5 we have plotted the values shown in Figure 2 for the rubber solutions measured by us according to the Umstaetter system. It can be seen that the measured points for both concentrations do, in fact, fall practically on a straight line. What is problematical in this, however, is the fact that it is practically never possible to take the values for η_0 and η_{∞} as they are given by experiment, but must approximate them by trial. Even though admittedly the determination of η_{∞} experimentally is not always a simple matter, nevertheless in every case the values of η_0 and η_{∞} so obtained have more the character of adjustable constants than that of exactly defined physical quantities. For the practical problem, however, this fact plays no decisive role, for the essential

feature of this representation is that the ratio of η_0 to η_∞ is chosen as a unit of the measure employed, in order to become independent of the characteristics of the dissolved molecules which are involved in η_0 and η_∞ (concentration, molecular weight). The adjustment of η_0 and η_∞ corresponds to the choice of the appropriate scale of measurement. Thus we are inclined in this sense to look on the Umstaetter representation as an empirical one, in spite of the fact that it was based by its originator on theoretical considerations. Nevertheless, even if it contains only what is expected of it in the practical sense, that is, if it actually makes it possible to represent the flow curves of a system as a single straight line, then certainly, for this reason alone, it can be called a useful advance in rheology.

The critical velocity gradient \hat{D} (at 50 per cent) for our rubber occurs at $1.5 \times 10^4 \text{ sec.}^{-1}$. This same value is found as the points of inflection of the two flow curves in Figure 2. Thus to our molecular weight of 830,000 corresponds a \hat{D} value of 1.5×10^4 . Unfortunately there are only very few such pairs of values available in the literature. Besides our own measurements, we were able to find data only by Philippoff and by Umstaetter. These three values are given in Table 1. As one can see, \hat{D} decreases with increasing $[\eta]$, which is certainly a measure of the molecular weight.

TABLE 1

$[\eta]$	\hat{D}
4	1.5×10^4
5	1.0×10^4
40	2.1×10^3

According to a more recent publication of Edelmann⁵, the straight lines obtained by the Umstaetter method are no longer influenced by the molecular weight of the sample. It is natural, therefore, to employ its steepness or a magnitude proportional to it as a measure of the lack of uniformity (polymolecularity) of the sample. It would be both fascinating and simple to explore this question experimentally.

In conclusion, let us say a few more words about the influence of the non-uniformity on the flow curves. It is known that it has as yet not been possible to formulate a universal flow law for solutions of high polymer substances, that is, a formula which gives the experimentally obtained flow curves unambiguously and without additional assumptions. This need not surprise us, since in fact we never have the possibility of measuring homogeneous (in a molecular sense) substances. It might nevertheless turn out that our measured flow curve, according to the particular non-uniformity of the sample, deviates more or less from the ideal flow curve, namely, that of a substance made up of molecules of a single size. If we knew the ideal flow curve, then the deviation from it would be a direct measure of the non-uniformity. It is a question, therefore, of collecting illustrative examples of the flow curves of uniform substances. This could be done by means of measurements of carefully fractionated samples, on substances prepared by special procedures in such a way as to produce uniform polymolecularity, or of model substances.

REFERENCES

- ¹ Schulz, *Z. Elektrochem.* **43**, 478 (1937).
- ² Staudinger, Joseph, and Leopold, *Ann. Chem.* **488**, 150 (1931); Staudinger, *Organ. Koll. Chem.*, Vieweg, Braunschweig 1950, page 212.
- ³ Carter, Scott, and Magat, *J. Am. Chem. Soc.* **68**, 1480 (1946).
- ⁴ Umstaetter, "Strukturmechanik, Leipzig, Steinkopff", 1948; "Einführung in die Viskosimetrie und Rheometrie", Berlin: Springer, 1952.
- ⁵ Edelmann, *Faserf. und Textiltech.* **5**, 59 (1954).

SLIPPING OF MOLECULES DURING THE DEFORMATION OF REINFORCED RUBBER *

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RUBBER-FILLER BONDS

There is much evidence now that a great many bonds of different energy content are present in rubbers reinforced by fillers. Presumably there are primary (chemical) bonds of at least two different types: (a) those formed by sulfur vulcanization¹ between the rubber molecules and the carbon black surface; (b) those formed in the reaction² between free radicals in the rubber molecules and the reinforcing fillers.

Moreover there are supposed to exist secondary (adsorption) bonds, which may vary in strength from the very low to the high order strength of primary bonds. Smith and Schaeffer³ have shown by adsorption experiments that energies of at least 20 kcal./mole are involved in physical adsorption, but there are reasons to assume⁴ that these values can be substantially larger due to steric conditions on the surface of the crystalline lattices, which lattices are present⁵ to an extent of about 70-90 per cent in carbon black.

RUPTURE OF BONDS DURING DEFORMATION

It is a well known fact⁶ that, after prestretching a piece of reinforced rubber, the stress-strain curve differs from that obtained on the first extension. This is called the Mullins effect. The curve approaches that of a pure-gum stock as the number of prestretches increases.

This Mullins effect is usually attributed to a breaking of bonds between rubber and filler⁷. An analysis⁸, based on this bond rupture theory, for natural rubber reinforced by carbon black is illustrated in Figure 1. It is obvious that the weak secondary bonds especially are broken during small extensions.

RESTORATION OF BONDS

There is one observation which does not fit this theory very well, namely, the extremely slow restoration of these broken bonds on resting. Figure 2 represents experiments by Mullins⁶, which show that, even at a temperature of 100° C, it takes something like 100 hours for complete recovery, which we interpret now as a restoration of the original bonds. These are neither in accord with the heat of wetting between hydrocarbons and black as measured by Smith and Schaeffer³ with the fact that carbon gel is formed readily at room temperature⁹.

* This is Communication No. 299 (1955) from the Rubber-Stichting. It was translated from the German by the author, and was prepared for publication in RUBBER CHEMISTRY AND TECHNOLOGY by E. C. Gregg, Jr.

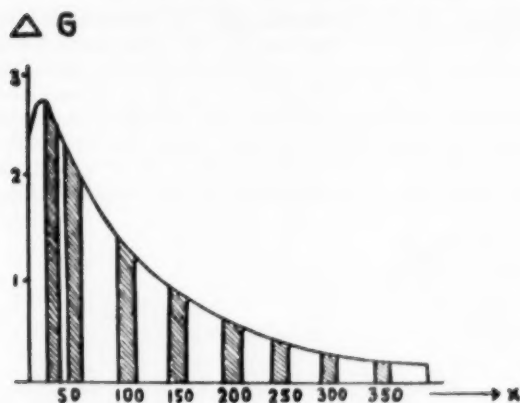


Fig. 1.—Strength distribution of secondary rubber-filler bonds. ΔG Number of bonds between x and x_1 . x Bond strength.

SLIPPING OF MOLECULES AND SPONTANEOUS RESTORATION OF BONDS

It seems possible to explain these observations by assuming that not only slipping of molecules over the surface of the filler takes place during deformation, but that, immediately afterwards, new bonds are formed of a nature similar to the original ones.

Such a reversible rupture of bonds is in accord with the general nature of physical bonds, and the only change occurring on stretching would be that the new bonds are at places on the rubber molecules different from the previous ones.

Figure 3 illustrates this slipping mechanism.

Figure 3a shows a coiled molecule at rest of which part BC is too short to cover the distance $B'C'$. If the attachment to the filler at B and C is by secondary bonds only, rupture of these bonds will occur, followed by slipping over

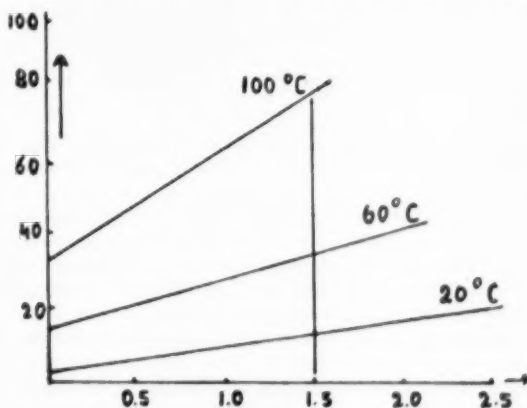


Fig. 2.—Recovery from the Mullins effect of a vulcanizate containing 50 per cent MPC black. The ordinate represents the percentage recovery; the abscissa represents the \log_{10} of the recovery time in hours.

the surface at B and (or) C. Hence the part BC of the molecule will become longer to cover the distance B'C' at the expense of the parts AB and CD.

On release of stress, (Figure 3c), the molecule will coil again but there is no reason why slipping at B' and C' should occur in the opposite direction because the tension in the molecule disappears from the very moment of release of stress.

When stressing the test-piece for a second time over the same distance, no slipping of the part B''C'' will take place because B''C'' already has the exact length required. The stress (modulus) during the second stretch will now be

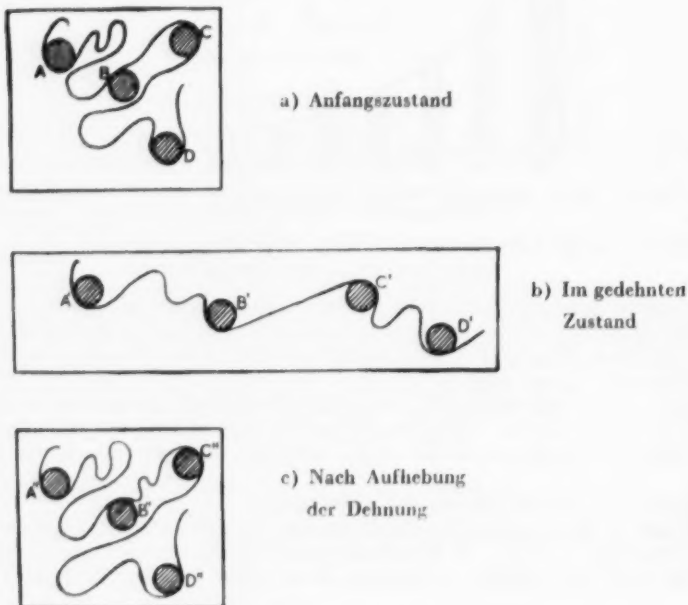


FIG. 3.—Mechanism of slipping.

- (a) Original state.
- (b) Stretched.
- (c) After release of the stress.

found equal to that of pure gum, i.e., the stress¹⁰ required to bring the molecules out of their statistically coiled position. This is exactly what is found in the Mullins effect.

As a matter of fact this "pure-gum modulus" is not found before, say, four cycles, showing that the situation of Figure 3b is not established immediately.

When stretching the molecule beyond the initial extension, new parts of the molecule come into the same position as part BC in the beginning and thus a successive slipping occurs throughout the material.

Now the question will be discussed as to how recovery to the original state occurs on resting.

From a thermodynamical viewpoint, the situation of Figure 3c is distinguished from the original state in so far as the entropy is lower than it would be if the rubber molecules were to return exactly to their original position.

An increase in temperature will result in a tendency to restore the original state of maximum entropy, and this is considered to be the factor controlling the restoration after the Mullins effect. There is a tendency to restore the original bonds, that is, to restore a state of equilibrium.

In the previous discussion the existence of primary filler-rubber bonds was neglected. If such bonds exist, their strength determines whether they will

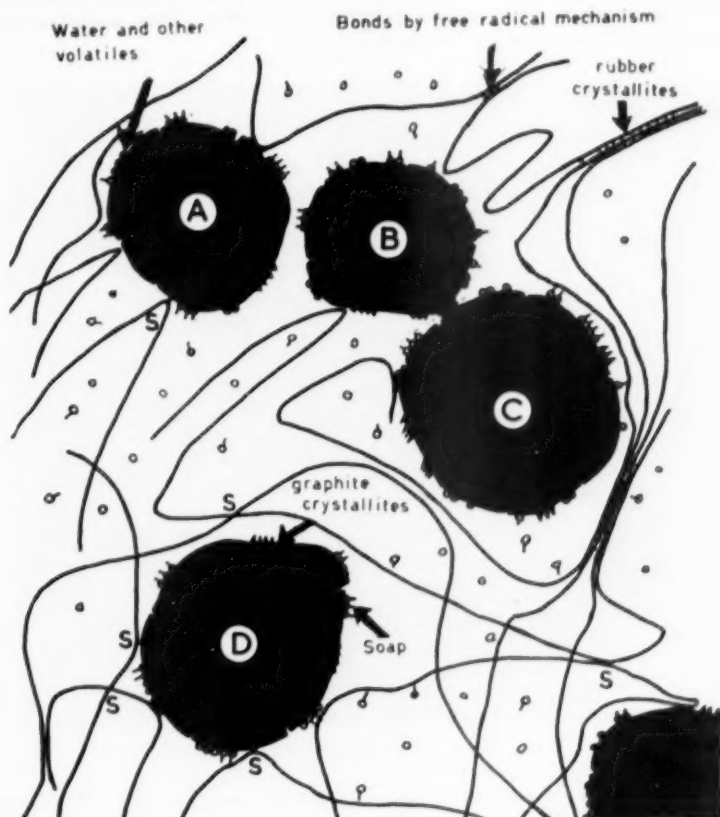


FIG. 4.—Schematic picture of a rubber vulcanizate containing 20 volume-per cent of EPC black. B and C are aggregates of carbon black particles; the other particles are freely dispersed.

break during deformation. This type of rupture will produce an irreversible contribution to the Mullins effect. Because the restoration of this sort of bonding can occur only by chemical reaction, this rupture therefore represents a permanent contribution to the Mullins effect.

If no breaking at all of the primary bonds occurs, there will be no irreversible contribution to the Mullins' effect. In fact Mullins' experiments clearly show that, after predeformation, the moduli of loaded stocks are still higher than those of the corresponding pure-gum vulcanizates. Consequently it may be assumed

that at least some of the primary bonds are not broken during prestressing. However, experiments regarding changes of internal energy during deformation¹¹ which might give information on this point, contradict each other¹².

The next question is whether there is sufficient room on the filler surface to make possible the proposed slipping. Data at hand indicate a degree of occupation of the carbon black surface which still leaves sufficient free room for slipping. Thus, vulcanization¹ leads to one S atom per 500 Å; the free radical mechanism² leads to one bond per 50–100 Å; adsorption of soap leads to a maximum of 15 per cent of coated surface.

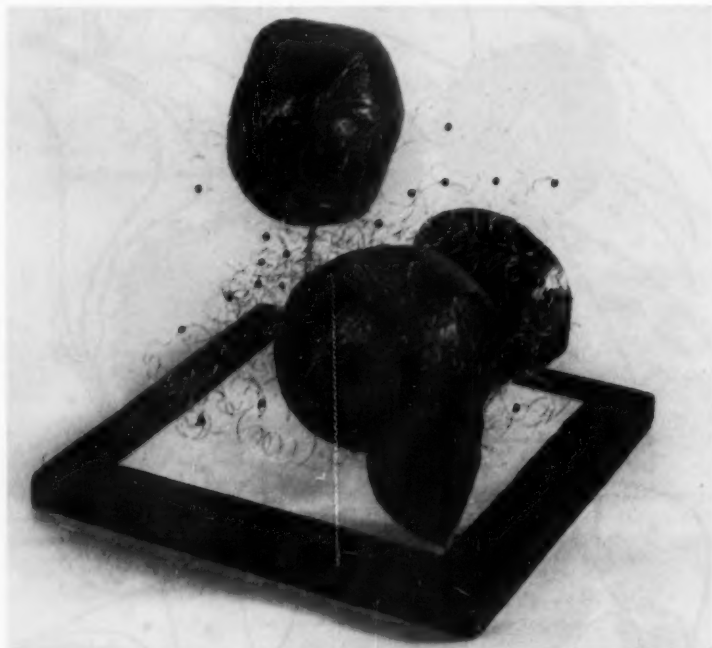


FIG. 5.—Model of rubber loaded with carbon black.

Figure 4 represents a picture based on the above assumptions. The largest carbon black particles in this picture have a diameter of 150 μ , while the smallest have a diameter of 30 μ . It is assumed that chinks and holes are present in the carbon black particles in order to explain the ratio between the surface area found by nitrogen adsorption and by means of the electron microscope.

Most of the volatile material (water) is presumed to be present in these crevices because of the greater energy increase ascribed to this type of adsorption⁶.

The soap molecules are assumed to be adsorbed preferentially head-down on the black; the tails are supposed to be parallel in bundles.

Figure 5 is a picture of a model constructed according to the principles shown in Figure 4.

According to this model it appears that the possibilities for slipping of rubber molecules over the surface of carbon black, as illustrated in Figure 3, are numerous. This model represents a tread compound loaded with 20 per cent by volume of EPC black (Spheron-9, particle diameter 300 Å). The wire represents one rubber chain of 9000 isoprene units (total length, 45,000 Å). This is only 1 per cent of the amount of rubber which should be present.

The small knots on the wire indicate where this chain may be imagined to be linked by sulfur bonds to the other chains.

SUMMARY

It is proposed that, during the deformation of reinforced rubber, the molecules slide along the surface of the filling material, accompanied by breaking of bonds. However, new bonds of similar type are soon formed (reversible breaking of bonds).

It is assumed that, in the quiescent state following deformation, the original bonds are eventually restored (disappearance of the Mullins effect); the increase of the entropy is supposed to be the effective source of energy.

A model of reinforced rubber is shown in Figure 5.

REFERENCES

- ¹ Stearns and Johnson, *Ind. Eng. Chem.*, **43**, 146 (1951).
- ² Garten and Sutherland, *Proc. Third Rubber Technol. Conf.*, London 1954, p. 536; Endter, *Kautschuk u. Gummi*, **5**, WT-17 (1952); Watson, *Proc. Third Rubber Technol. Conf.*, London 1954, p. 553.
- ³ Smith and Schaeffer, *Proc. Second Rubber Technol. Conf.*, London 1948, p. 403.
- ⁴ Houwink, *J. Polymer Sci.*, **4**, 763 (1949).
- ⁵ Studebaker, Paper presented at the 123rd meeting of the American Chemical Society, 1954.
- ⁶ Mullins, *J. Rubber Research*, **16**, 275 (1947).
- ⁷ Blanchard, *Proc. Third Rubber Technol. Conf.*, London 1954, p. 592.
- ⁸ Blanchard, *J. Polymer Sci.*, **14**, 355 (1954).
- ⁹ Sweitzer, *Rubber Age*, **72**, 55 (1952).
- ¹⁰ Its statistical position will have altered and consequently its entropy has changed. This alteration, however, is of the same order of magnitude as entropy effects in pure-gum stocks.
- ¹¹ Stearns and Johnson, *Ind. Eng. Chem.*, **43**, 146 (1951); Schytil and Volpers, *Kolloid.-Z.*, **130**, 110 (1953).
- ¹² The results mentioned (Schytil and Volpers, *Kolloid.-Z.*, **130**, 110 (1953)) are obviously based on the thesis of R. Volpers, Frankfurt/M., 1951. In his experiments, the tension seems not to have been determined under equilibrium conditions because of incomplete relaxation. The calculated energy and entropy terms seem, therefore, insufficiently reliable (remarks by M. M. Horikx, Delft).

THE LIMITING VALUE OF DITHIOCARBAMATE FORMATION DURING THE VULCANIZATION OF NATURAL RUBBER WITH THIURAM DISULFIDES *

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DETERMINATION OF ZINC DITHIOCARBAMATE

As is well known, we have determined the zinc dithiocarbamate which is formed during the vulcanization of natural rubber. Our procedure involves conductometric titrations with hydrochloric acid of aqueous acetone solutions of the residues which are obtained by extraction. In the course of necessary preliminary studies¹, we have shown that this type of titration of the dithiocarbamate is also feasible in the presence of tetraalkylthiuram disulfide.

However, we have asked ourselves whether only the zinc dithiocarbamate formed during vulcanization is determined unaffected by fortuitously present impurities in the acetone-extracted pale crepe. Therefore we have set up a series of experiments in which we have determined the zinc dithiocarbamate content of vulcanizate extracts by two methods. In one procedure we used the conductometric method. In the other we measured the zinc salt content by potentiometric titration with standard alkali. If only the dithiocarbamate is determined unaffected by impurities, then the two methods should yield concordant results.

It should be emphasized that agreement is always found for fully cured vulcanizates. The electrometric titration of the zinc in extracts of undercured vulcanizates containing unreacted thiuramdisulfide, however, tends to give too high values for the zinc dithiocarbamate, because the thiuram disulfide, which is sensitive towards bases², may cause a somewhat high consumption of alkali if the titration is carried out slowly³ (Einstellung der Potentiale).

Figure 1 shows a series of potentiometric titration curves of zinc with standard alkali in extracts of various vulcanizates. The added caustic in ml. is plotted on the abscissa against the millivoltmeter readings on the ordinate. In order to show all the curves in one diagram, they are horizontally transposed; yet, by considering the divisions it is easy to read on the abscissa the amount of alkali which is used for the precipitation of the zinc as hydroxide between the potential jumps a and a' . The concordance of the potentiometric and conductometric titrations is evident from the text under Figure 1.

Therefore we come again to the conclusion that, during the acidometric conductometry of the extracts from thiuram vulcanizates, only the dithiocarbamate which is formed during the cure is determined quantitatively.

Furthermore, the formation of zinc dithiocarbamate during vulcanization can be very easily demonstrated qualitatively. Thus, during the concentration

* Translated by Franz Widmer for RUBBER CHEMISTRY AND TECHNOLOGY from portions of an article in *Kautschuk und Gummi* Vol. 9, No. 2, WT27-30, February 1956. The parts omitted are mostly concerned with comments by the authors on a thesis by H. W. Zijp⁴, who previously had commented on the work of Scheele and others⁵.

of the extracts colorless crystals (needles) precipitate. After filtration and recrystallization, they show the melting point of the particular zinc dithiocarbamate. In order to be sure, we convinced ourselves from time to time. Finally, on addition of an aqueous solution of copper sulfate, all the extracts of thiuram vulcanizates immediately give a brown-red precipitate of copper dithiocarbamate, or a solution with such a color in the extracting medium if this is not miscible with water.

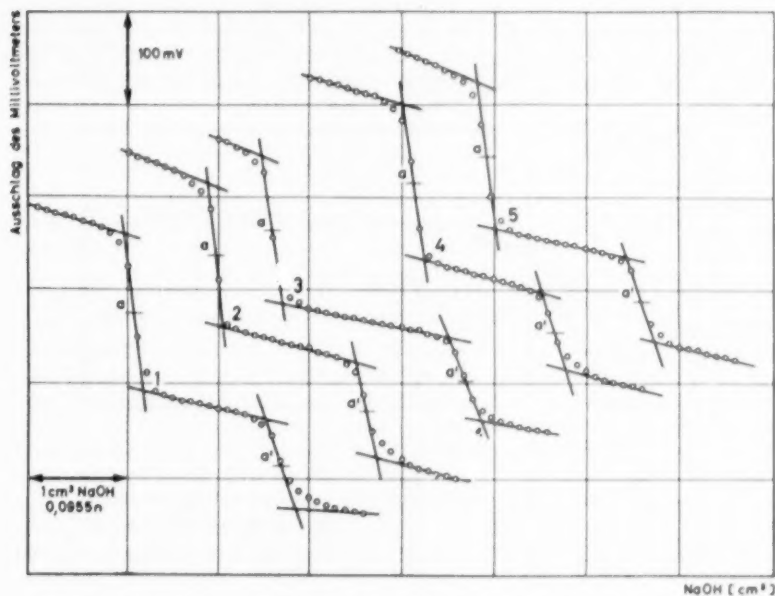


FIG. 1.—Electrometric titration curves of zinc with standard alkali. The zinc was liberated by acid treatment of zinc dithiocarbamate in vulcanization extracts (glass electrode).

	Conductometric	Potentiometric
Curve 1	40.39 mg.	40.11 mg.
Curve 2	11.91 mg.	12.19 mg.
Curve 3	25.51 mg.	25.75 mg.
Curve 4	37.00 mg.	37.42 mg.
Curve 5	19.86 mg.	20.16 mg.

EXTRACTION OF THIURAM VULCANIZATES AND THE LIMITING VALUE OF DITHIOCARBAMATE FORMATION

In the first communication of this series⁶ we pointed out that tetraalkylthiuram disulfides slowly decompose in boiling organic solvents; and according to newer researches in our institute, if zinc oxide is present, the corresponding zinc dithiocarbamate may be formed. If no zinc oxide is present, the respective dialkylamines are liberated. The decomposition of the thiuram disulfides depends on the type of solvent and proceeds at different rates; e.g., at a higher rate in acetone than in cyclohexane; and among the three tetraalkylthiuram disulfides which we investigated, the decomposition of the tetramethylthiuram disulfide proceeds faster than that of the two next higher homologs. Finally

it should be mentioned that exposure to light accelerates decomposition, and therefore solutions, especially those of tetramethylthiuram disulfide, are not completely stable when exposed to light, even at room temperature.

From these observations, which are supported by many analyses, it must be concluded that it is not advisable to extract thiuram vulcanizates with boiling acetone; and this is especially true for those products which are obtained by vulcanization with tetramethylthiuram disulfide. Generally better results are obtained if boiling cyclohexane is used. But especially with respect to a quantitative determination of the remaining thiuram disulfide in not completely cured stocks hot extractions should not be employed. The situation is different if one wants to restrict the extraction to the zinc dithiocarbamate which has been formed. But in this case also, accurate quantitative results are not obtained.

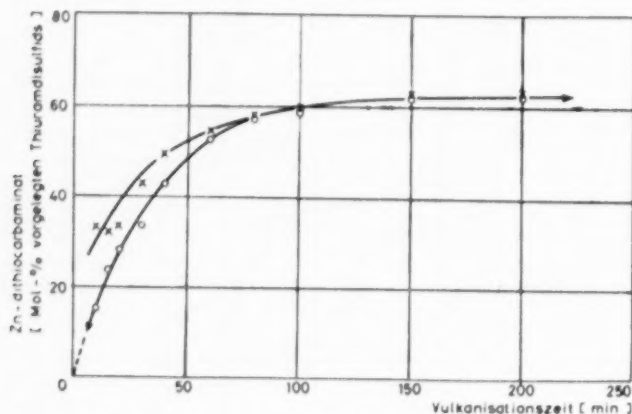


Fig. 2.—Vulcanization of natural rubber with tetraethylthiuram disulfide. Formation of zinc dithiocarbamate in relation to time at 140° C. Crosses: hot extraction. Circles: cold extraction.

It has been proved quantitatively by a large number of investigations in our laboratory that, during the extraction of vulcanizates with boiling solvents, curing continues. Therefore the yields for a particular time and temperature are too high and the consumption of thiuram disulfide, if at all measurable, is found to be too high.

For this very reason, when the quantitative analysis of the extracts had to be used for a study of the reaction kinetics during the thiuram vulcanization, we have always extracted the vulcanizates with ethyl acetate⁷ in the dark at room temperature.

Out of the abundance of the available research material we chose a vulcanizate at random and plotted the reaction curve for results (Figure 2) obtained from both hot and cold extraction. It can be seen that, especially in the region of short cure times, the curve of hot extraction (crosses) differs from the curve of cold extraction (circles); the quantitative analysis gives too high results for the zinc dithiocarbamate during hot extraction. It can also be recognized that the differences between the curves become less significant with rising time of cure and finally disappear. This is very important with respect to the following explanations, which we have verified in many cases⁸.

From this it follows that, with respect to the formation of zinc dithiocarbamate

ate, the cure always leads to one, and only one, limiting value. It is immaterial whether the temperature of curing chosen is substantially above 100° C, with subsequent extraction at a lower temperature with a boiling solvent (in which vulcanization continues), or at room temperature in the dark, where the cure has practically come to a stop.

We now have demonstrated that vulcanization with a thiuram disulfide always leads—practically independent of the temperature and the constitution of the tetraalkylthiuram disulfide—to 66 mole-per cent of zinc dithiocarbamate, no matter whether the vulcanizates are extracted with boiling acetone or with ethyl acetate at room temperature in the dark². In other words, the limiting value of the yield of dithiocarbamate is independent of the type of extraction.

But because the two extraction methods in question give different results with vulcanizates not completely cured (see Figure 2), cold extraction is preferred. This is what we always did in obtaining the analytical data during our study of the kinetics of thiuram vulcanization.

H. W. Zijp evidently extracted his thiuram vulcanizates and also the masticates with boiling acetone. According to the preceding explanations, and with consideration of Figure 2, it is clear that in this manner he obtains too large an amount of zinc dithiocarbamate, especially from extraction of the masticates. If he concludes that zinc dithiocarbamate is formed during the mixing operation, he is doubtless in error, since it is well established that, during extraction with boiling solvents, vulcanization and, therefore, formation of dithiocarbamate, takes place. It is thus uncertain whether or not dithiocarbamate is formed during the mixing operation. Nevertheless, his opinion is right in so far as dithiocarbamate may be formed during mixing. This will depend on the mixing temperature and on the time required to mix the thiuram disulfide. But he is really in no position to conclude from his researches whether, and to what extent any reaction takes place during mixing.

Apart from such considerations, as will be shown later, the amount of zinc dithiocarbamate formed during mixing, at least in our investigations, is very small. If one takes into account what has been said in connection with the relationships expressed in Figure 2, it is obvious that, for the limiting value of dithiocarbamate formation, it is quite immaterial whether or not some reaction has already taken place during mixing, and is unimportant for the limiting value whether extraction was with boiling solvents, whereby a certain post-cure takes place, or at room temperature in the dark, whereby a post-cure is practically impossible. In other words, if a slight precure during mixing has an influence on the limiting value of dithiocarbamate formation, the temperature of extraction should reflect its influence on the limiting value of dithiocarbamate formation. But this is not the case, as we have seen. Expressed differently, since during hot extraction and, circumstances permitting perhaps during mixing, the same reaction takes place, namely, the formation of a certain amount of dithiocarbamate at a temperature which is different from the temperature of cure, a reaction during mixing should have no effect on the limiting value of dithiocarbamate formation, because hot extraction also is without influence.

Although it is without question of no importance for the limiting value of the dithiocarbamate formation, if the reaction between thiuram disulfide and rubber begins during mixing, we have, nevertheless, chosen the reaction conditions for the preparation of the masticates in such a manner that a possible reaction is kept at a minimum. We have kept the working temperature as low as possible (mostly at 30 to 40° C), and we did the mixing in the shortest possible time. As a matter of fact, the dithiocarbamate formed during mixing is only slight.

This may be seen in particular if the decreasing concentration of the thiuram disulfide during cure is plotted versus percentage reaction. This is a first-order reaction, and the plot is a straight line far beyond a 50 per cent range of the reaction, and it cuts the ordinate practically at 100 per cent, although it has to be admitted that an effect which may be caused by precure also could be compensated by the unavoidable warm-up period of the molds in the thermostat. But if an appreciable reaction had already taken place during the warm-up period, the straight lines certainly would not cut the ordinates at 100 per cent, but at clearly measurable values below 100 per cent. We have observed such a behavior many times during cure with benzoyl peroxide¹⁰. However, for a first-order reaction, this in reality indicates merely a transposition of the time axis.

As is well known, we have also investigated the cure of natural rubber with tetramethylthiuram monosulfide and sulfur¹¹, by choosing a ratio of one mole of monosulfide per gram-atom of sulfur. Here again, practically independent of the temperature, 66 mole-per cent of the thiuram monosulfide was transformed into zinc dithiocarbamate when the curing temperatures were 120° and higher. At lower temperatures the limiting values were noticeably higher. This is undoubtedly associated with the dependence of the vulcanization kinetics on the reaction of the monosulfide with sulfur, which precedes curing. In this connection it should be mentioned that, in the absence of sulfur, the thiuram monosulfide also forms zinc dithiocarbamate in a very slow reaction with rubber. This reaction is possibly noticeable also at lower curing temperatures if thiuram monosulfide and sulfur are used¹². Since, in the low-temperature range, the rate constant of dithiocarbamate formation depends on the temperature, it may be concluded, for the case in question, that no reaction of the reactants with rubber can take place during mixing¹¹. In spite of this, it was observed that the limiting value of dithiocarbamate formation, which is practically independent of the temperature, at least at higher temperatures (120° C and above), where the cure proceeds quantitatively like the thiuram disulfide cure, is 66 mole-per cent of the monosulfide added. Furthermore, as long as the proportions of the monosulfide and sulfur added correspond to the composition of the disulfide, we infer that the cure is essentially a disulfide cure.

Finally, in connection with all this, we would like to recall our investigations with the model compound, geraniol. We found that the entire reaction between tetraethylthiuram disulfide and an excess of geraniol under nitrogen again gave 66 mole-per cent of zinc dithiocarbamate, practically irrespective of the temperature. These investigations were carried out in such a manner that the thiuram disulfide was added to a solution of geraniol in xylene when the solution had reached the desired temperature. In this case, something which could correspond to a precure during the milling of rubber cannot occur at all; yet we find in every respect the same effects as those in the thiuram vulcanization of rubber.

THE DEPENDENCE OF THE LIMITING VALUE OF DITHIOCARBAMATE FORMATION ON THE CONCENTRATION DURING THE VULCANIZATION OF RUBBER WITH TETRAALKYLTHIURAM DISULFIDE

Even in our first investigations on thiuram vulcanization, we obtained the impression that the limiting value of the yield of dithiocarbamate is not only practically independent of vulcanization temperature, but also is practically constant within a wide range of concentrations of thiuram disulfide. However,

we have always emphasized in publications and lectures that a thorough investigation of the limiting value as a function of the thiuram disulfide concentration has still to be made. Indeed, such investigations have been in progress for a short time. The results are shown¹² in Table I.

In Table I, columns 1 and 2 show the concentration of the thiuram disulfide (for the case in question that of tetraethylthiuram disulfide) in millimoles or grams, respectively, per 100 grams of the mixture. In this series of experiments, the concentration was varied in the ratio of 1:6. Columns 3 and 4 indicate the amount of zinc oxide in millimoles or grams, respectively, contained in 100 grams of mixture. Whereas in earlier experiments we employed a 5-fold excess of zinc oxide, we now chose a 12-fold excess, and for Experiment No. 5 even a 24-fold excess. In this way, it was possible to ascertain simultaneously whether a change of the zinc oxide ratio affects the limiting value. The result of these experiments was as follows. Although the amount of zinc oxide employed rises rapidly with rising concentration of the thiuram disulfide added, and the amount of rubber decreases correspondingly, the limiting value of dithiocarbamate formation still is 66 per cent of the thiuram disulfide added.

TABLE I
VULCANIZATION OF NATURAL RUBBER WITH TETRAETHYLTHIURAM
DISULFIDE AT 120° C AND AT VARIOUS CONCENTRATIONS OF
ZINC OXIDE AND OF TETRAETHYLTHIURAM DISULFIDE

Tetraethylthiuram disulfide		Zinc oxide			Natural rubber Grams per 100 g. of mixture	Limiting value of the dithiocarbamate
Milli- moles in 100 g. of mixture	Grams per 100 g. of mixture	Milli- moles in 100 g. of mixture	Grams per 100 g. of mixture	Molar excess of zinc oxide		
5	1.48	61.5	5.0	12.3	93.52	66 mole-per cent of thiuram disulfide added
7.5	2.22	92.1	7.5	12.3	90.28	
10	2.96	123	10	12.3	87.04	
10	2.96	246	20	12.3	77.04	
20	5.92	246	20	24.6	74.04	
30	8.88	369	30	12.3	61.12	

With respect to the degenerated (entartet) composition of the mixture when larger amounts of zinc oxide are added, one may, indeed, speak of an independence of the limiting value from the concentration in a not insignificant range of the change of concentration of the thiuram disulfide in rubber.

These results are confirmed by the investigations of the dependence of the limiting value of dithiocarbamate formation on the concentration of tetraethylthiuram disulfide with geraniol during the reaction. In a series of experiments carried out at 122.5° C, the concentration of thiuram disulfide was varied over the ratio of 1:4 (0.9 to 3.6 g. of tetraethylthiuram disulfide per 20 ml. of geraniol). It could be demonstrated that the limiting value in all cases amounts to 66 mole-per cent of the thiuram disulfide added. The dithiocarbamate values found for each concentration with respect to time fell on a single reaction curve.

It is evident that the limiting value of dithiocarbamate formation is independent of the concentration. In spite of this, we shall continue our studies in order to show whether or not the reaction of tetraalkylthiuram disulfides with rubber is stoichiometric. It would also be of interest to know whether the kinetics of dithiocarbamate formation change when the concentration of thiuram

disulfide in rubber is changed (whereby the zinc oxide additions have to be increased or decreased, respectively).

SUMMARY

This paper disproves an assertion by H. W. Zijp that a fundamental result of our investigations was wrong. The result in question is that the limiting value of dithiocarbamate formation (66 mole-percent of the thiuram disulfide added) is independent of the temperature and, in a certain range, is also independent of the concentration of thiuram disulfide, added. It is shown experimentally that a reaction of thiuram disulfide with rubber which may take place fortuitously during mixing cannot be of any influence on the limiting value of the dithiocarbamate formation.

REFERENCES

- ¹ Zijp, H. W., "Topassing Van De Papierchromatographie Bij De Identificatie Van In De Rubberindustrie Gebruiklijke Versnellers En Antioxydantien", Delft, 1955.
- ² Scheele, Lorenz, and Dummer, *Kautschuk u. Gummi*, **7**, WT 273 (1954); **8**, WT 2, 27 (1955); Scheele and Lorenz, *Kautschuk u. Gummi* **8**, WT 85 (1955); Scheele and Bielstein, *Kautschuk u. Gummi* **8**, WT 251 (1955).
- ³ Scheele and Gensch, *Kautschuk u. Gummi* **6**, WT 147 (1953).
- ⁴ Scheele and Gensch, *Kautschuk u. Gummi* **7**, WT 122 (1954).
- ⁵ The measurements were carried out by means of a glass electrode.
- ⁶ Scheele, Lorenz, and Dummer, *Kautschuk u. Gummi* **7**, WT 275 (1954).
- ⁷ We extracted especially with ethyl acetate, not only because it is a good solvent for the compounds which have to be analyzed in thiuram vulcanizates, but can also be used pure enough to assure unobjectionable conductometric titrations.
- ⁸ For additional data, see Scheele, Lorenz, and Dummer, *Kautschuk u. Gummi* **8**, WT 2 (1955). The analytical results form a fairly smooth curve only if the time periods for the hot extractions are kept constant.
- ⁹ Scheele, Lorenz, and Dummer, *Kautschuk u. Gummi* **7**, WT 272 (1954); **8**, WT 2 (1955).
- ¹⁰ Lorenz and Scheele, *Kautschuk u. Gummi* **8**, WT 273 (1955). See the following paper.
- ¹¹ Scheele and Bielstein, *Kautschuk u. Gummi* **8**, WT 251 (1955).
- ¹² Unpublished work by Scheele and Bielstein.
- ¹³ Incomplete investigations by Scheele and Stange.

STUDIES OF THE VULCANIZATION OF ELASTIC HIGH POLYMERS. VI. THE VULCANIZATION OF NATURAL RUBBER WITH BENZOYL PEROXIDE.

PART 1 *

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INTRODUCTION AND STATEMENT OF THE PROBLEM

In the latest communication of this series¹ we pointed out in particular that the results of our previous investigations of the vulcanization of natural rubber by thiuram disulfides could not be brought into agreement with the prevailing view, according to which vulcanization is finally brought about by sulfur. Without being ready at this point to reject completely our earlier interpretation, we are rather inclined to discuss a reaction with the rubber of free radicals, $=N-C(S)-S^*$. An interaction of these free radicals (or molecular fractions) with both the double bonds and the α -methylene groups should, we believe, be discussed on the basis of our experimental findings. In our opinion, thiuram vulcanization brings about a linking of the polyisoprene chains by C—C bonds.

For this reason we are interested also in the kinetics of the vulcanization of natural rubber by peroxides, especially by benzoyl peroxide, which is frequently employed as a chain starter in polymerization kinetics, and concerning whose type of reaction with compounds containing double bonds more is known. On this basis it can only be assumed that it cross-links rubber by C—C bonds.

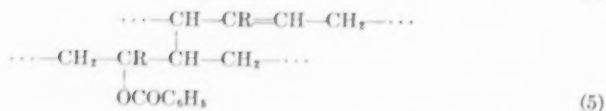
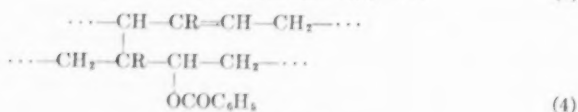
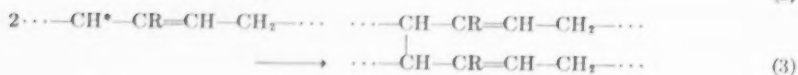
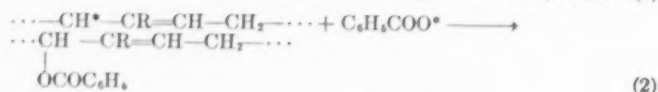
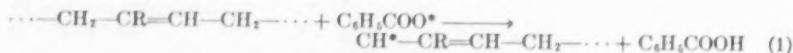
The vulcanization of natural rubber by peroxides has been the object of considerable study, but less, to be sure, with respect to its kinetics than with the aim of learning the physical-technical properties² of peroxide vulcanizates and the characteristic features of this vulcanization reaction. Nevertheless some effort has been made to gain a deeper insight into peroxide vulcanization by studying the interaction of peroxides with model compounds, e.g., cyclohexene, and by isolating and identifying the resulting end products.

Now it should be pointed out at the outset that vulcanization by benzoyl peroxide will hardly find any practical application, since really useful vulcanizates are obtained only when one works with very large additions of peroxide. This is the opposite of thiuram vulcanization, for even slight additions of thiuram disulfide to the mix produce high-quality vulcanizates. In spite of such a difference in the effectiveness of these two vulcanization agents, however, a comparison of the kinetics of their reaction with rubber seems interesting and worthwhile. This is because, although they give different results with respect to the physical properties of the vulcanizates, they are able to react with rubber in a fundamentally identical manner. The correctness of this idea is supported by the fact that di-*tertiary*-butyl peroxide, whose interaction with rubber we have not yet been able to study, produces much better vulcanizates³, although its interaction with rubber will certainly be quite analogous.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by D. W. Kitchin from *Kautschuk und Gummi*, Vol. 8, No. 11, pages WT 273-280, November 1955.

Farmer and Michael⁴ studied the reaction of benzoyl peroxide with cyclohexene at 140° C, and found among the reaction products benzoic acid, carbon dioxide, various hydrocarbons with 6 or 12 carbon atoms (cyclohexane, benzene, and cyclohexenyl cyclohexene) as well as various benzoates of these hydrocarbons, especially cyclohexyl-, cyclohexenyl-, and cyclohexenyl-cyclohexyl benzoate. About half of all the available benzoyloxy radicals become combined in the reaction products. This agrees with the observations of van Rossem, Dekker, and Prawirdipero⁵ in the vulcanization of natural rubber with benzoyl peroxide, according to which a considerable portion of the peroxide goes over into benzoic acid and the vulcanizate contains benzoyloxy groups in firm combination (benzoate groups). The results of the studies of the interaction of benzoyl peroxide with the model substance cyclohexene have led Farmer and Michael to attribute the vulcanization of rubber with benzoyl peroxide to the following reaction mechanism.

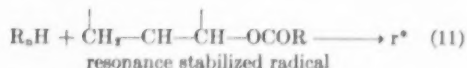
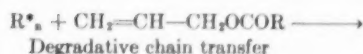
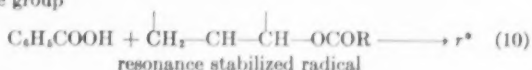
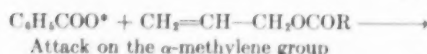
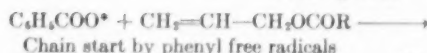
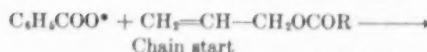
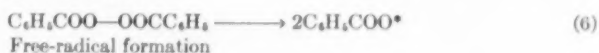
The benzoyloxy radicals react principally with the α -methylene groups of the structural units of the polyisoprene chains, with the formation of benzoic acid (1) and at the same time produce chain free radicals which then become saturated according to (2) by benzoyloxy free radicals, or else combine in pairs (3), which gives cross-linking (vulcanization). There is further discussed a combination of the chain radicals according to (1) with free radicals which can arise from addition of benzoyloxy radicals to the double bonds. Structures (4) and (5) are considered to be especially probable.



Since in the meantime we have found that thiuram disulfide reacts likewise with allyl acetate with respect to the kinetics in exactly the same manner as with geraniol or with rubber⁶, our growing interest has been aroused in the investigations of Bartlett and Altschul⁷, who concerned themselves with the polymerization of allyl acetate initiated with benzoyl peroxide. The results they obtained and the conclusions drawn by them might well be significant for the discussion of the relationships found in peroxide vulcanization.

In the polymerization of allyl acetate induced by benzoyl peroxide, in which oils of high viscosity are produced, there is also formed an appreciable amount of benzoic acid. The peroxide disappears according to a reaction of the first order, and there is a linear relation between the amount of it which is converted

and the decrease of the monomer (allyl acetate). The experiments lead to the assumption of a chain breaking by the monomer. The following reactions are discussed by Bartlett in detail:



combination of the resonance stabilized radicals

The benzoyloxy radicals formed in (6) attach themselves to the double bonds of the monomer and create a substituted radical of the monomer (7), that gives rise to a polymerization (8) in the chain. Chain start as well as chain growth, however, can also be effected by phenyl radicals (9). The course of this reaction can be inferred from the observation of carbon dioxide produced during the polymerization. In this process the benzoyloxy radical is not only a chain starter, but is also able to react with the α -methylene groups of the allyl acetate (10). This produces benzoic acid and a resonance stabilized radical, which is not capable of starting a chain but rather combines with its own type (12). It is of importance that Bartlett and Altschul also consider possible an interaction of the chain radical formed in reaction (8) with the monomer involving the formation of that resonance stabilized radical (11). This signifies a chain termination by the monomer and is designated by them as "degradative chain transfer".

While it is not possible to make a direct determination of the number of cross-links produced per mole of the vulcanizing agent in vulcanization by peroxides (this is generally true of any vulcanization), which would correspond to the customary determination of the amount of the polymer or to the measurement of the decrease of concentration of the monomer in the analysis of an ordinary polymerization, one can nevertheless study the kinetics of the formation of the benzoic acid. This, however, is not directly possible in the case of the polymerization of allyl acetate.

The present paper reports the results obtained in the chemical investigation of the vulcanization of natural rubber by benzoyl peroxide. The study in-

volved the kinetics of the decrease of the peroxide and of the formation of benzoic acid at different temperatures and concentrations of the peroxide in the rubber.

EXPERIMENTAL

The experiments were carried out with pale crepe (acetone-extracted) in the same manner as in the case of the thiuram vulcanization, except that the peculiar characteristics of the benzoyl peroxide had to be taken into consideration. Since the peroxide reacts appreciably with rubber even at rather low temperatures, the temperature of the mill rolls was maintained as low as possible during the mixing. Addition of zinc oxide is unnecessary, since the benzoic acid formed is absolutely stable at the vulcanization temperatures. Moreover, even when zinc oxide is added, no zinc benzoate whatever is formed. This may be a consequence of the association shown by benzoic acid in nonpolar solvents.

The characteristics of peroxide vulcanizates, which are extensively described in the literature, were also to be observed in our products. Vulcanizates of short reaction times are at first transparent, but become cloudy after a short time (a few minutes), yet no crystals separate out on their surface. Exhaustively reacted vulcanizates remain transparent even on standing. Vulcanizates obtained with relatively small amounts of peroxide are tacky, have only slight elasticity, and appear to change but slightly on standing for many weeks. With increasing concentration of peroxide the tackiness decreases, and the vulcanizates show greatly improved elasticity.

Vulcanizates made with large additions of peroxide incompletely reacted quickly become cloudy again (separation of peroxide), while completely reacted ones are transparent. However, a few hours after their preparation, crystals of benzoic acid separate out on their surface. On longer standing even vulcanizates made with high peroxide concentration become tacky or develop cracks according to the progress of the vulcanization. These purely qualitative observations are understandable when one considers the fact that benzoyl peroxide is also able to degrade rubber.

In the individual vulcanizates the peroxide and the benzoic acid were determined quantitatively.

For the analysis of benzoyl peroxide we used two methods. One of them, developed by Nozaki⁸, was employed to obtain the peroxide content of weakly cross-linked vulcanizates, while the other, which was proposed by Siggia⁹, was used for the determination of the peroxide in strongly cross-linked vulcanizates prepared by the addition of larger amounts of peroxide.

In carrying out the method of Nozaki, the extraction of the vulcanizate with acetic anhydride was carried out at room temperature for 5-6 days in the dark. Five to 10 cc. of the extract, which was brought to a definite volume and in some cases concentrated in vacuum, was thoroughly shaken with 200 mg. of powdered potassium iodide. After 5-10 minutes, 50-75 cc. of distilled water was added. After the solution had again been vigorously shaken for some time, the separated free iodine was titrated with 0.02 normal thiosulfate solution.

With strongly cross-linked vulcanizates, even a five-day extraction with acetic anhydride was not sufficient to dissolve out all the peroxide from the vulcanizate. In fact, some times this took twice as long. In such cases the extraction was made with acetone at room temperature, and the peroxide in the extract was determined by the method of Siggia. In this procedure a measured

TABLE 1
CONDUCTOMETRIC TITRATION OF BENZOIC ACID
WITH NaOH AT 45° C

Wt. in mg. benzoic acid	Calcd. cc. 0.1N NaOH	Found cc. 0.1N NaOH	Deviation (%)
6.1 0.05 millimole	0.50	0.50	0
		0.515	3.0
		0.505	1.0
		Av. 0.507	Av. 1.4
9.15 0.075 millimole	0.75	0.75	0
		0.75	0
		0.74	-1.4
		Av. 0.747	Av. -0.5
12.2 0.1 millimole	1.00	0.99	-1.0
		0.985	-1.5
		1.00	0
		Av. 0.992	Av. -0.8

amount of extract, diluted with water, if necessary, to a definite volume, was treated with 2-4 cc., depending on the estimated amount of the peroxide, of a 0.05 normal solution of arsenious oxide and about 100 mg. of sodium bicarbonate. It was brought to boiling, and care was taken to evaporate out the acetone. After this operation the solution was neutralized with 1 normal sulfuric acid in order to destroy the sodium carbonate. Then sodium bicarbonate was again added, and finally the solution was titrated back with 0.5 normal solution of iodine in potassium iodide to determine the excess arsenious acid (starch indicator).

TABLE 2
CONDUCTOMETRIC TITRATION OF BENZOYL PEROXIDE
WITH NaOH AT 45° C

Wt. in mg. benzoyl peroxide	Calcd. cc. 0.1N NaOH	Found cc. 0.1N NaOH	Deviation (%)
6.06 0.025 millimole	0.50	0.51	2.0
		0.51	2.0
		0.52	4.0
		Av. 0.513	Av. 2.6
12.11 0.05 millimole	1.00	1.005	0.5
		1.005	0.5
		1.00	0.0
		Av. 1.003	Av. 0.3
18.17	1.50	1.495	-0.3
		1.505	0.3
		1.515	1.0
		Av. 1.505	Av. 0.3
24.22 0.1 millimole	2.00	1.97	-1.5
		1.99	-0.5
		2.00	0.0
		Av. 1.987	Av. -0.7

The determination of the benzoic acid could be made only indirectly, and this was done to best advantage by conductometric titration. It is known that solutions of benzoic acid can be readily titrated conductometrically with sodium hydroxide. One obtains the typical pictures for weak acids. In Table 1 a number of the analytical results are shown. We next convinced ourselves that the peroxide also can be titrated conductometrically with sodium hydroxide. It is expedient to do this at somewhat higher temperature, e.g., 45° C. However, the reaction takes place with measurable velocity, so it is necessary, after each addition of alkali, to wait for the galvanometer to reach a constant deflection. Table 2 gives values showing the precision of this method

TABLE 3
CONDUCTOMETRIC TITRATION OF A MIXTURE OF BENZOIC ACID (BS)
AND BENZOYL PEROXIDE (BP) WITH NaOH AT 45° C

Wt. in mg. benzoic acid (BS) and benzoyl peroxide (BP)	Calcd. cc. 0.1N NaOH	Found cc. 0.1N NaOH	Deviation (%)
6.06 BP	0.75	0.77	2.7
3.05 BS		0.77	2.7
		0.76	1.3
		Av. 0.767	Av. 2.2
6.06 BP	1.00	1.01	1.0
6.10 BS		1.02	2.0
		1.01	1.0
		Av. 1.013	Av. 1.3
6.06 BP	1.25	1.24	-0.8
9.15 BS		1.23	-1.6
		1.22	-2.4
		Av. 1.23	Av. -1.6
6.06 BP	1.50	1.50	0
12.20 BS		1.52	1.3
		1.48	-1.3
		Av. 1.50	Av. 0

of determining the benzoyl peroxide. Unfortunately it is not possible to titrate the benzoic acid in the presence of benzoyl peroxide, for the reaction of the peroxide does not take place slowly enough, even at lower temperatures, to avoid making the recognition of the titration end point uncertain. For this reason it was necessary to obtain the sum of both by conductometric titration with sodium hydroxide and, from the difference between this sum and the result of the peroxide determination, to arrive at the benzoic acid content of the vulcanizate. That one obtains sufficiently accurate results for the sum, peroxide plus benzoic acid, is shown in Table 3.

THE EXPERIMENTAL RESULTS AND THEIR DISCUSSION

The vulcanization of natural rubber by benzoyl peroxide takes place much more rapidly than the thiuram vulcanization. In order, therefore, to work in an experimentally favorable region, it was studied at the temperatures 110°, 90°, 75°, 60°, and 50° C.

Table 4 gives the results of the quantitative analysis of the vulcanizates obtained at each of these temperatures. A more detailed interpretation of the table is superfluous and is omitted.

We first show in Figure 1 the decrease of concentration of the peroxide with time at the five temperatures. As would be expected, the curves drop more steeply the higher the temperature. But none of them intersects the ordinate for 100 per cent, as should be the case. This implies that, even during the mixing, the benzoyl peroxide reacts to a marked extent with the rubber, al-

TABLE 4
PEROXIDE DECREASE AND BENZOIC ACID INCREASE IN THE REACTION OF NATURAL RUBBER WITH BENZOYL PEROXIDE. DEPENDENCE ON TEMPERATURE AT CONSTANT CONCENTRATION

Initial amounts: 100.0 g. natural rubber, 2.0 g. benzoyl peroxide.

50° C			60° C			75° C		
Time (min.)	Peroxide (mol-%)	Benzoic acid (mol-%)	Time (min.)	Peroxide (mol-%)	Benzoic acid (mol-%)	Time (min.)	Peroxide (mol-%)	Benzoic acid (mol-%)
0	92.0	5.3	0	82.3	10.0	0	85.3	6.7
270	76.8	14.8	90	71.4	16.0	30	69.4	12.2
510	67.3	20.4	180	63.2	20.2	60	58.2	16.4
870	56.2	26.7	270	56.9	23.1	90	45.6	20.3
1380	44.3	33.7	360	47.5	27.9	120	38.5	24.3
1860	36.2	39.5	450	42.0	31.8	150	31.8	27.8
2400	26.9	44.4	540	38.4	33.1	180	23.1	30.0
2850	21.0	46.3	840	24.6	37.9	240	16.3	34.6
4800	9.5	54.8	1260	13.1	45.1	360	7.6	41.7
7200	(2.8)	58.6	1560	8.7	47.9	480	3.3	42.3
			2280	2.6	50.6	720	0.5	47.5
			3060	—	54.2	1080	—	47.3
∞		60.0	∞		55.0	∞		48.0

90° C			110° C		
Time (min.)	Peroxide (mol-%)	Benzoic acid (mol-%)	Time (min.)	Peroxide (mol-%)	Benzoic acid (mol-%)
0	87.0	7.8	0	87.2	9.1
15	56.4	19.3	5	61.2	18.0
30	37.5	25.5	10	26.5	25.1
45	24.6	30.6	15	12.1	33.5
60	17.2	33.7	20	5.5	37.1
75	10.7	37.7	25	1.3	39.4
90	6.2	39.3	30	0.9	40.3
120	3.0	42.8	90	—	41.8
180	0.4	44.6	180	—	42.2
240	—	46.1	360	—	43.4
			840	—	45.0
∞		47.0	∞		45.0

though the temperature of the mill rolls was kept as low as possible. This is not a hindrance in the evaluation of the experimental results, however, for Figure 2 (abscissa: vulcanization time t in minutes; ordinate: log mole-per cent peroxide) shows that the decrease of peroxide content at all temperatures and over the whole range of the observed reaction times is of the first order. The velocity constants K_{BP} are shown in Table 5.

Now whereas the peroxide decreases with the time of reaction, the benzoic acid content of the vulcanizate increases, as shown by Figure 3 (abscissa: vulcanization time t in minutes; ordinate: concentration of the benzoic acid in

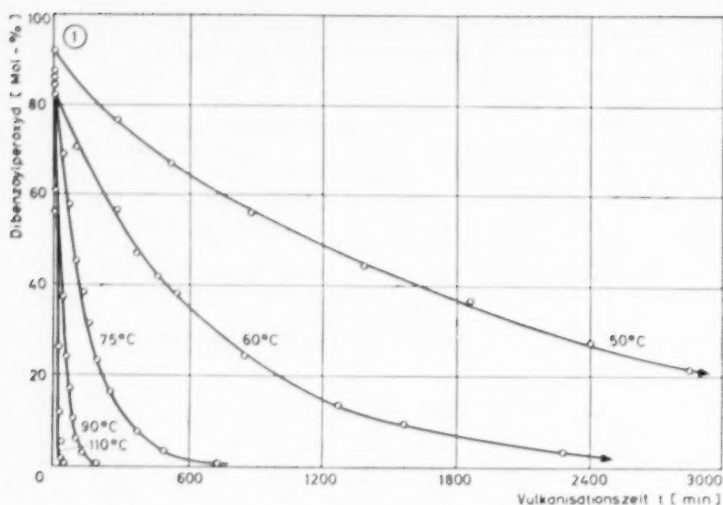


Fig. 1.—Decrease of concentration of benzoyl peroxide with vulcanization time. Ordinate: benzoyl peroxide in mole-per cent; abscissa: vulcanization time in minutes.

mole-per cent of the added peroxide). The slope of the curves is steeper the higher the temperature. These relationships correspond to the increase of concentration of dithiocarbamic acid (zinc dithiocarbamate) with time in thiuram vulcanization¹⁰. However, whereas there the final yield of dithiocarbamate amounts to about 66 per cent, practically independent of the tem-

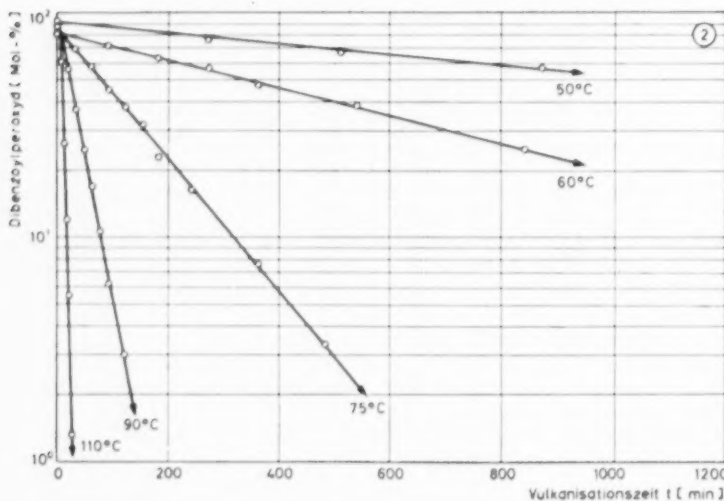


Fig. 2.—Decrease of concentration of benzoyl peroxide in its reaction with rubber as a reaction of the first order. Ordinate: benzoyl peroxide in mole-per cent; abscissa: vulcanization time in minutes.

TABLE 5
REACTION VELOCITY CONSTANTS OF THE PEROXIDE DECREASE IN THE
INTERACTION OF NATURAL RUBBER WITH BENZOYL PEROXIDE

50° C		60° C		75° C		90° C		110° C	
Time (min.)	$K_{BP} \cdot 10^4$ (min. ⁻¹)	Time (min.)	$K_{BP} \cdot 10^4$ (min. ⁻¹)	Time (min.)	$K_{BP} \cdot 10^4$ (min. ⁻¹)	Time (min.)	$K_{BP} \cdot 10^4$ (min. ⁻¹)	Time (min.)	$K_{BP} \cdot 10^4$ (min. ⁻¹)
270	4.59	90	1.58	30	6.86	15	2.88	5	1.61
510	5.05	180	1.47	60	6.37	30	2.81	10	1.64
870	5.03	270	1.36	90	6.95	45	2.81	15	1.62
1380	4.88	360	1.53	120	6.59	60	2.70	20	1.61
1860	4.72	450	1.49	150	6.57	75	2.79	25	(1.86)
2400	4.89	540	1.41	180	7.24	90	2.93	Av.	1.62
2850	4.98	840	1.43	240	6.89	120	2.80		
4800	4.61	1260	1.46	360	6.71	Av.	2.81		
7200	4.77	1560	1.44	480	6.76				
Av.	4.80	2280	1.51	Av.	6.77				
		Av.	1.47						

perature, the limiting value of the benzoic acid formation in peroxide vulcanization is evidently not constant, for the curves of Figure 3 intersect. Here again one can arrive at the limiting value by plotting the concentration of the benzoic acid vs. the reciprocal of the time of vulcanization. This method of presenting the experimental results will be omitted here to save space. The limiting values obtained in this manner can be found from Table 1. It is seen that they decrease with rising temperature of vulcanization. From this it could be concluded that, with increasing temperature, benzoyl peroxide reacts more and more by a side reaction. For example, one might propose the splitting off of carbon dioxide from the benzoyloxy radicals. This would result in a lessening of the yield of benzoic acid as a consequence. But van Rossem and his coworkers have not been able to show production of any carbon dioxide in peroxide vulcanization, and we too have up to now been unable to produce any proof of its formation. Nevertheless, we should like to leave open for the present the question of the eventual formation of carbon dioxide and also the discussion of the temperature dependence of the limiting value.

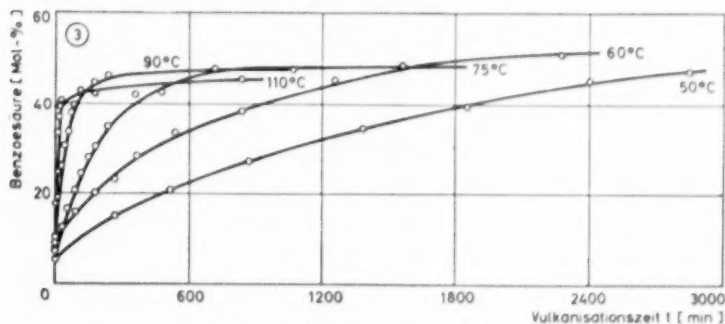


FIG. 3.—Increase of concentration of benzoic acid with vulcanization time.
Ordinate: benzoic acid in mole-per cent.

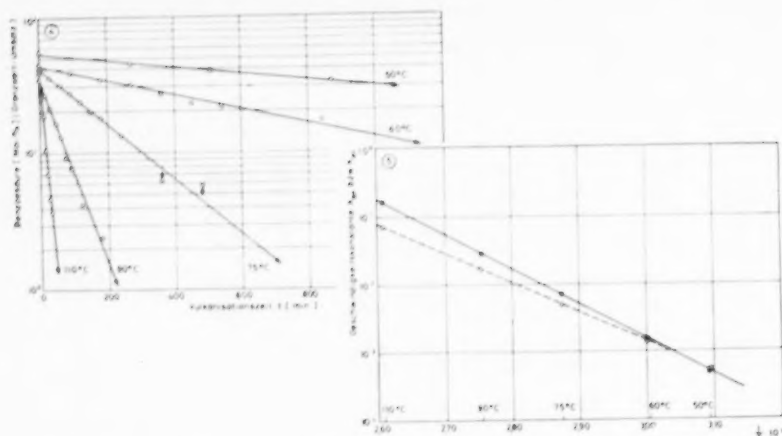


FIG. 4.—Formation of benzoic acid in the vulcanization of natural rubber by benzoyl peroxide as a reaction of the first order. Ordinate: benzoic acid in mole-per cent (limiting value of conversion); abscissa: vulcanization time in minutes.

FIG. 5.—Effect of temperature on the velocity constants of peroxide decrease K_{BP} and benzoic acid formation K_{BA} . ● Benzoyl peroxide, ○ benzoic acid. Ordinate: velocity constants K_{BP} and K_{BA} ; abscissa: $(1/T) \times 10^3$.

If one takes the difference between the limiting value and the concentration of benzoic acid (in mole-per cent of the added peroxide) and plots the logarithm vs. the vulcanization time t , one obtains, as shown by Figure 4, straight lines over the whole experimental range. From this it follows that the formation of benzoic acid can also be characterized as a first-order reaction. In this feature it resembles the formation of the dithiocarbamate in thiuram vulcanization. The velocity constants K_{BS} of the benzoic acid formation for the different temperatures can be taken from Table 6. If one compares the figures there with those of Table 5, one notes immediately that the formation of benzoic acid at

TABLE 6
REACTION VELOCITY CONSTANTS OF THE BENZOIC ACID (BA) FORMATION
IN THE INTERACTION OF NATURAL RUBBER WITH BENZOYL PEROXIDE

50° C		60° C		75° C		90° C		110° C	
Time (min.)	$K_{BA} \cdot 10^4$ (min. ⁻¹)	Time (min.)	$K_{BA} \cdot 10^4$ (min. ⁻¹)	Time (min.)	$K_{BA} \cdot 10^4$ (min. ⁻¹)	Time (min.)	$K_{BA} \cdot 10^4$ (min. ⁻¹)	Time (min.)	$K_{BA} \cdot 10^4$ (min. ⁻¹)
270	5.24	90	1.60	30	4.72	15	1.71	5	5.82
510	5.27	180	1.51	60	4.55	30	1.73	10	6.03
870	5.17	270	1.38	90	4.48	45	1.73	15	7.52
1380	4.98	360	1.46	120	4.66	60	1.66	20	7.71
1860	5.03	450	1.50	150	4.76	75	1.78	25	7.77
2400	5.03	540	1.39	180	4.63	90	1.70	30	7.27
2850	4.73	840	1.21	240	4.68	120	1.78	Av.	7.02
4800	4.82	1260	1.24	360	5.17	180	1.52		
7200	5.02	1560	1.22	480	4.16	240	1.55		
Av.	5.03	2280	1.05	720	6.07	Av.	1.68		
		3060	1.33	1080	(3.81)				
		Av.	1.36	Av.	4.79				

higher temperatures takes place much more slowly than the decrease of concentration of the benzoyl peroxide, but that the differences in the velocity constants of the two processes become less with decreasing temperature and disappear at 60° C; that is, at still lower temperatures the constants are identical. This becomes especially evident if one looks at the velocity constants in Figure 5 as a function of temperature (ordinate: logarithm of the velocity constants K_{BP} and K_{BS} ; abscissa: reciprocal of the absolute temperature). The course

TABLE 7
PEROXIDE DECREASE AND BENZOIC ACID INCREASE IN THE REACTION
OF NATURAL RUBBER WITH BENZOYL PEROXIDE. DEPENDENCE
ON THE CONCENTRATION AT 75° C

Composition					
100.0 g. Natural rubber 2.0 g. Benzoyl peroxide			98.0 g. Natural rubber 4.0 g. Benzoyl peroxide		
Time (min.)	Peroxide (mol-%)	Benzoic acid (mol-%)	Time (min.)	Peroxide (mol-%)	Benzoic acid (mol-%)
0	85.3	6.7	0	90.0	5.3
30	69.4	12.2	45	67.5	16.6
60	58.2	16.4	90	50.5	20.8
90	46.5	20.3	150	34.3	28.9
120	38.5	24.3	210	23.2	35.0
150	31.8	27.8	330	10.7	40.9
180	23.1	30.0	450	5.0	42.9
240	16.3	34.6			
360	7.6	41.7			
480	3.3	42.3			
720	0.5	47.5			
1080	—	47.3			

94.0 g. Natural rubber 8.0 g. Benzoyl peroxide			86.0 g. Natural rubber 16.0 g. Benzoyl peroxide		
Time (min.)	Peroxide (mol-%)	Benzoic acid (mol-%)	Time (min.)	Peroxide (mol-%)	Benzoic acid (mol-%)
0	95.0	3.9	0	95.2	3.3
40	77.0	9.3	40	85.7	8.7
80	57.1	16.5	80	76.2	12.1
140	38.1	26.0	120	65.0	19.2
200	25.1	32.2	160	52.7	24.5
280	14.9	37.6	200	40.5	30.6
370	8.4	42.0	260	25.7	34.8
440	5.6	43.6	300	17.1	37.2
540	3.0	44.6	400	10.3	41.2
680	—	47.1	460	7.0	43.4
900	—	47.8	520	4.1	44.2
			920	—	46.2
			1440		46.3

of the curves indicates that at lower temperatures the formation of benzoic acid should take place eventually faster than the decrease of peroxide. This is, of course, impossible, and therefore in this region the decrease of peroxide is the velocity-determining factor for the whole vulcanization process. That is, the temperature function of the velocity constants of benzoic acid formation here follows the temperature dependence of the velocity constants of the decrease of peroxide. At higher temperatures, however, the two reactions can be clearly distinguished with respect to their velocity, and the relationships are again analogous to those of thiuram vulcanization, in so far as there the decrease of

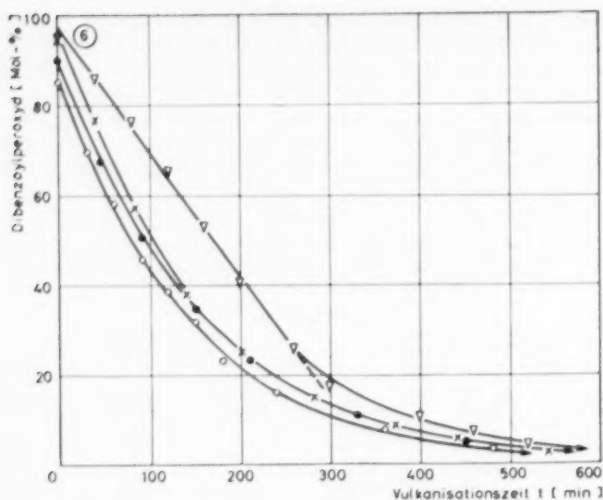


Fig. 6.—Decrease of concentration of benzoyl peroxide (BP) in rubber (NR) with vulcanization time at 75° C and different concentrations of peroxide.

○ 2.0 g. BP: 100.0 g. NR × 8.0 g. BP: 94.0 g. NR
● 4.0 g. BP: 98.0 g. NR ▽ 16.0 g. BP: 86.0 g. NR

Ordinate: benzoyl peroxide in mole-per cent. Abscissa: vulcanization time in minutes.

the thiuram disulfide occurs more rapidly than the increase of the dithiocarbamate. We must therefore assume that the mechanism of peroxide vulcanization involves an intermediate compound just like that of thiuram vulcanization. It must, however, also be pointed out that a study of peroxide vulcanization at temperatures below 60° C would not lead to such an assumption, since—to

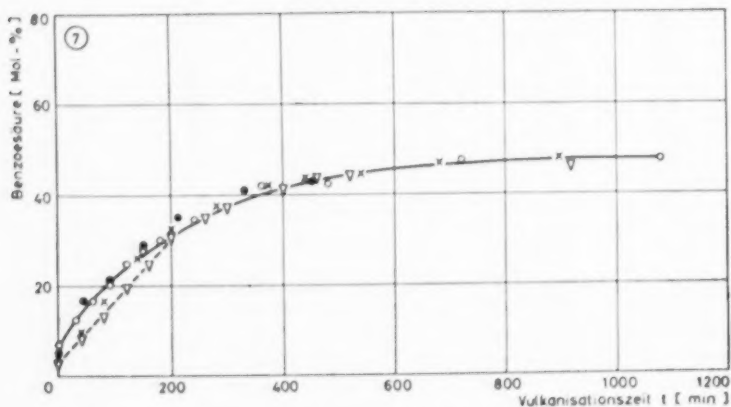


Fig. 7.—Increase in concentration of benzoic acid at 75° C in vulcanizates with different starting concentrations of peroxide.

○ 2.0 g. BP: 100.0 g. NR × 8.0 g. BP: 94.0 g. NR
● 4.0 g. BP: 98.0 g. NR ▽ 16.0 g. BP: 86.0 g. NR

stress this fact once more—at these temperatures both processes (peroxide decrease and benzoic acid formation) have the same velocity.

We also investigated the dependence on concentration of peroxide vulcanization, to be sure, at only one temperature, but up to additions of peroxide to rubber at which the reactions go over into ones of the zero order instead of the first order. This must, of course, always be the case when the solubility limit of the peroxide is exceeded.

Table 7, which needs no explanation, contains these results. Figure 6 shows the decrease of the peroxide with time (ordinate: peroxide in mole-per cent; abscissa: vulcanization time in minutes); Figure 7 the increase of concentration of the benzoic acid (ordinate: benzoic acid in mole-per cent of the added peroxide; abscissa: vulcanization time t in minutes).

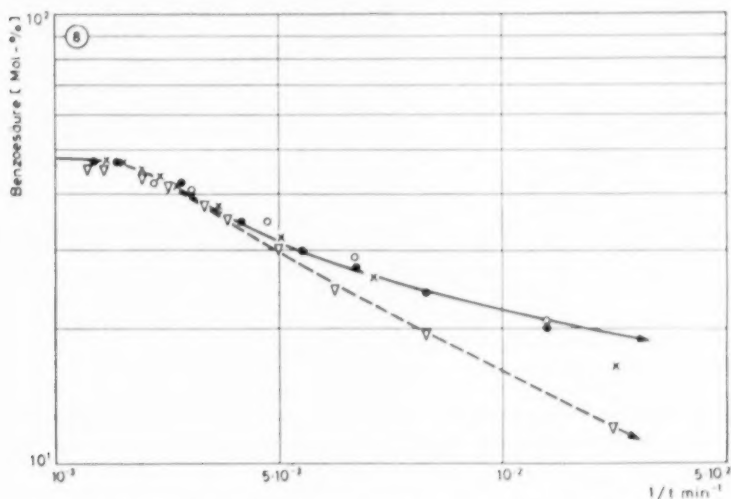


Fig. 8.—Demonstration of the dependence of the limiting value of benzoic acid formation on the concentration at 75°C.

○ 2.0 g. BP: 100.0 g. NR × 8.0 g. BP: 94.0 g. NR
● 4.0 g. BP: 98.0 g. NR ▽ 16.0 g. BP: 86.0 g. NR

Ordinate: benzoic acid in mole-per cent; abscissa: $1/t$ min.

The fact that the analytical data for the different additions of peroxide in Figure 6 do not fall on a single curve is a consequence of the interaction of the peroxide with the rubber, which starts even during the mixing in of the peroxide and is quantitatively uncontrollable. Only the linear decrease of the peroxide with eight-fold amount added shows a peculiarity in the range of times from $t = 0$ to $t = 260$ minutes. It indicates that with so high additions there is no longer any possibility of complete solubility, and for this reason the course of the reaction now follows the first order until the saturation of the rubber with peroxide is removed by its being used up. This is the case after about 260 minutes, as shown by the fact that, with longer vulcanization times, deviation from a linear course occurs. In the increase with time of the benzoic acid in Figure 7, the incipient conversion during the mixing shows up less markedly, for one can connect the analytical results in a curve, about which they oscillate.

But here too one observes in the region of relatively short vulcanization times and with high concentrations a linear relation between the benzoic acid concentration and the time, an indication of a zero-order reaction rate. It can be seen from Figure 8 (ordinate: log concentration of benzoic acid in mole-per cent; abscissa: reciprocal of the reaction time) that the limiting value of the benzoic acid formation is independent of the concentration, at any rate in the range here studied. Finally Figures 9 and 10 show that both the decrease of peroxide concentration and the formation of benzoic acid at all the concentrations in question are reactions of the first order, and that only at higher peroxide additions do deviations from this occur. This is a consequence of exceeding the

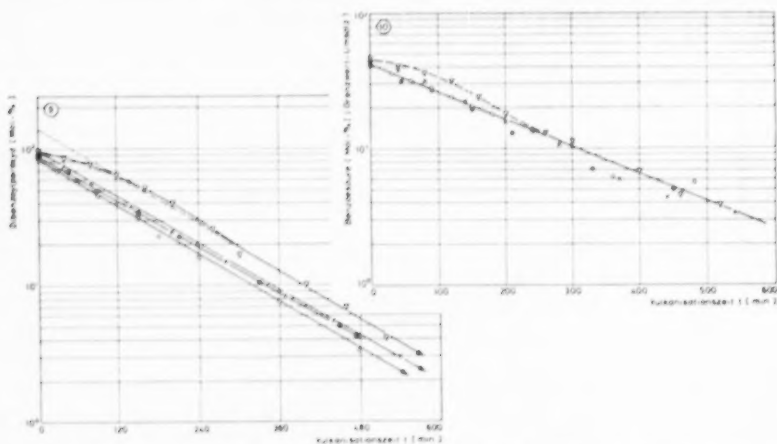


FIG. 9.—Peroxide decrease as a reaction of the first order at 75° C and different concentrations.

○ 2.0 g. BP: 100.0 g. NR × 8.0 g. BP: 94.0 g. NR
● 4.0 g. BP: 98.0 g. NR ▽ 16.0 g. BP: 86.0 g. NR

Ordinate: benzoyl peroxide in mole-per cent; abscissa: vulcanization time in minutes.

FIG. 10.—The formation of benzoic acid as a first-order reaction at 75° C and various concentrations.

○ 2.0 g. BP: 100.0 g. NR × 8.0 g. BP: 94.0 g. NR
● 4.0 g. BP: 98.0 g. NR ▽ 16.0 g. BP: 86.0 g. NR

Ordinate: benzoic acid in mole-per cent (limiting value of conversion); abscissa: vulcanization time in minutes.

solubility limits of the peroxide. The velocity constants given in Tables 8 and 9 for the two reactions are practically alike and in good agreement with the constants given in Tables 5 and 6 for the temperature of 75° C.

A remarkable result of the above investigation seems to us to be the existence of a formal analogy between peroxide and thiuram vulcanization with respect to their kinetic relationships. Both the thiuram disulfide and the benzoyl peroxide react with natural rubber according to a first-order reaction. In a reaction that proceeds more slowly at higher temperatures and according to the first order, benzoic acid or dithiocarbamic acid, respectively, are formed. In thiuram vulcanization, there is formed in every case 66 mole-per cent of dithiocarbamic acid, calculated on the added thiuram disulfide. In peroxide vulcanization, on the other hand, the final yield of benzoic acid depends on the reaction temperature and is smaller the higher this is.

TABLE 8
REACTION VELOCITY CONSTANTS OF THE PEROXIDE DECREASE IN THE
INTERACTION OF NATURAL RUBBER WITH BENZOYL PEROXIDE AT 75° C

Initial concentration of the peroxide (mol./kg.)							
0.081		0.162		0.324		0.648	
Time (min.)	$K_{RP} \cdot 10^3$ (min. ⁻¹)	Time (min.)	$K_{RP} \cdot 10^3$ (min. ⁻¹)	Time (min.)	$K_{RP} \cdot 10^3$ (min. ⁻¹)	Time (min.)	$K_{RP} \cdot 10^3$ (min. ⁻¹)
30	6.86	45	6.44	40	(5.35)	40	(1.23)
60	6.37	90	6.42	80	6.44	80	(7.62)
90	6.95	150	6.42	140	6.57	120	(6.40)
120	6.59	210	6.46	200	6.68	160	(6.10)
150	6.57	330	6.44	280	6.63	200	(6.20)
180	7.24	450	6.42	370	6.56	260	(6.51)
240	6.89	Av.	6.43	440	6.44	300	(7.00)
360	6.71			540	6.38	400	6.52
480	6.76			Av.	6.53	460	6.50
Av.	6.77					520	6.78
						Av.	6.60

The kinetic relationships, in our opinion, make it unavoidable to assume in both cases the formation of an intermediate compound. In the case of peroxide vulcanization, this conclusion emerges only as a result of the studies at the higher temperatures, for below 60° C both reactions become of equal velocity. Measurements at low temperatures can thus be misleading with regard to the true state of affairs. If one must postulate an intermediate compound, however, then there are difficulties in the way of bringing the reaction mechanisms proposed by Farmer and Bartlett into agreement with the experimental results. Each of the reaction paths discussed requires for every benzyloxy radical which reacts an allyl unit in order to form benzoic acid directly. The possibility of benzoic acid production exists only so long as there is peroxide still present.

TABLE 9
REACTION VELOCITY CONSTANTS OF THE BENZOIC ACID (BA) INCREASE IN THE INTER-
ACTION OF NATURAL RUBBER WITH BENZOYL PEROXIDE AT 75° C

0.081		0.162		0.324		0.648	
Time (min.)	$K_{BA} \cdot 10^3$ (min. ⁻¹)	Time (min.)	$K_{BA} \cdot 10^3$ (min. ⁻¹)	Time (min.)	$K_{BA} \cdot 10^3$ (min. ⁻¹)	Time (min.)	$K_{BA} \cdot 10^3$ (min. ⁻¹)
30	4.72	45	5.52	40	(2.97)	40	(2.75)
60	4.55	90	4.64	80	(3.76)	80	(2.61)
90	4.48	150	5.06	140	4.53	120	(3.37)
120	4.66	210	5.38	200	4.78	160	(3.72)
150	4.76	330	5.28	280	4.90	200	4.37
180	4.63	450	4.65	370	5.16	260	4.41
240	4.68	Av.	5.09	440	5.05	300	4.48
360	5.17			540	4.62	400	4.52
480	4.16			680	5.57	460	4.77
720	6.07			900	5.87	520	4.58
Av.	4.79			Av.	5.06	920	(3.45)
						1440	(2.27)
						Av.	4.52

Thus unfortunately we cannot apply to peroxide vulcanization the plausible deductions which Bartlett makes from his investigations on allyl acetate. In this present case it seems that there must be different relationships than those involved in the peroxide induced polymerization of allyl acetate. But we now also think that the reaction path developed by Farmer for peroxide vulcanization still does not quite hit the mark.

SUMMARY

The vulcanization of natural rubber by benzoyl peroxide between 110° and 50° C has been investigated. The analysis of the kinetics has led to the following results:

1. The benzoyl peroxide concentration decreases at all temperatures according to a reaction of the first order. The velocity constants have been given.
2. Benzoic acid is formed in a slower reaction, but also according to a first order rate. The limiting value of benzoic acid formation depends on the temperature. It decreases with increasing temperature. The velocity constants for benzoic acid formation have been calculated.
3. With larger additions of peroxide to the rubber, both reactions are of the zero order as long as the solubility limit of the peroxide is exceeded.
4. The temperature dependence of the velocity constants of both reactions has been discussed, and it has been shown that at lower temperatures the formation of benzoic acid and the decrease of peroxide become equally rapid.
5. The analogy between thiuram vulcanization and peroxide vulcanization with respect to their kinetics has been pointed out.
6. It has been made apparent that, in both peroxide vulcanization and thiuram vulcanization, one is obliged to assume the formation of an intermediate compound. But, at the same time, it is not possible to make this consistent with the reaction mechanism which Farmer has developed for peroxide vulcanization, nor to apply to peroxide vulcanization the relationships found by Bartlett for the polymerization of allyl acetate by benzoyl peroxide.

ACKNOWLEDGMENTS

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REFERENCES

- ¹ Scheele and Bielstein, *Kautschuk u. Gummi* **8**, WT 251 (1955).
- ² For example, Braden, Flechter, and McSweeney, *RUBBER CHEM. AND TECHNOL.* **28**, 190 (1955).
- ³ Farmer and Moore, *J. Chem. Soc.* **152**, 142 (1951).
- ⁴ Farmer and Michael, *J. Chem. Soc.* **143**, 513 (1942).
- ⁵ Van Rossem, Dekker, and Prawirdiposro, *Kautschuk* **7**, 202 (1931); *RUBBER CHEM. AND TECHNOL.* **5**, 97 (1932).
- ⁶ Lorenz and Scheele, unpublished experiments. On the reaction of geraniol, as a model compound, see Scheele and Lorenz, *Kautschuk u. Gummi* **8**, WT 85 (1955).
- ⁷ Bartlett and Altschul, *J. Am. Chem. Soc.* **67**, 812, 816 (1945).
- ⁸ Nozski, *Anal. Chem.* **18**, 583 (1946); Houben-Weyl, 4. Ed., Vol. 2, p. 574.
- ⁹ Siggia, *Anal. Chem.* **19**, 827 (1947).
- ¹⁰ Scheele, Lorenz, and Dummer, *Kautschuk u. Gummi* **7**, WT 273 (1954); **8**, WT 2, 27 (1955).

THE THEORY OF VULCANIZATION AND THE ACTION OF ACCELERATORS *

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INTRODUCTION

The fundamental step of the vulcanization process is the formation of chemical cross-links between the molecular chains of the rubber. The presence of these bonds is responsible for the principal differences between vulcanized rubber and crude rubber—lack of solubility, final value of the equilibrium modulus of elasticity, and impossibility of passage into a liquid state without destruction of the chemical bonds. The formation of chemical cross-links can take place as a result of the following reactions: (1) reactions between the rubber molecules and the biradicals or bifunctional groups characteristic of the vulcanizing agent; (2) secondary reactions between the functional groups of one molecule formed during vulcanization and the double bonds of another; (3) secondary reactions between the functional groups of various molecules formed during vulcanization and metal oxides or other oxidizing agents contained in the vulcanized mixture; (4) thermal or thermal oxidation structure formation of the rubber. The reaction between the double bonds and the sulfur biradicals S_2^* or dithiols, $HSRSH$, is an example of the first type of reaction¹. The second type is observed in the reaction between the double bonds of the sulfhydryl groups formed in the rubber molecules as a result of primary reactions with sulfur, and the accelerator and hydrogen sulfide². The third reaction occurs between the sulfhydryl and carboxyl groups of the various molecular chains and metal oxides, sulfur, and oxygen³. The fourth reaction was studied in an earlier work⁴.

A theory of the development of polymerization processes induced by the free radicals formed by the vulcanizing agent during vulcanization, leading to the formation of $-C-C-$ bonds between the molecular chains of the rubber, was proposed by the authors. However, no evidence of the existence of such processes was obtained; furthermore, a number of data (for example, data from the spectral analysis of a vulcanizate) contradicted this assumption. The present study is devoted to a description of experiments which illuminate this very essential aspect of the vulcanization process.

REACTION BETWEEN RUBBER AND BENZOTHAZOLYL DISULFIDE

In one of the preceding studies, Dogadkin and Feldshtein⁵ observed the independent vulcanizing action of two widely used vulcanization accelerators: dibenzothiazolyl disulfide and benzothiazole sulfenamide in heating various

* Translated from RUBBER CHEMISTRY AND TECHNOLOGY from *Kolloidnyi Zhurnal*, Vol. 17, No. 3, pages 215-219 (1955). Most of the data used in this study appeared in the Thesis of V. V. Selyukova, completed in the Moscow Institute of Fine Chemical Technology, from 1950 to 1953. A brief report of this work appeared in *Doklady Akademii Nauk S.S.S.R.* 92, 61 (1953).

mixtures of rubber with these compounds at 143° . The vulcanizing action depends on the type of rubber: it is least apparent in the case of natural rubber⁶; benzothiazolyl disulfide reacts most intensively on sodium-butadiene rubber, and benzothiazole sulfendiethylamide on butadiene-styrene rubber. The dynamics of the change of tensile strength and residual deformation during heating of a mixture containing 100 parts by weight of sodium-butadiene rubber, 50 parts of channel carbon black and 5 parts of benzothiazolyl disulfide, and a similar mixture containing 2.6 parts of sulfur is shown as an illustration in Figure 1. As is seen, benzothiazolyl disulfide has a stronger vulcanizing action in this case than the classic vulcanizing agent, sulfur.

The action of benzothiazolyl disulfide was then studied by heating toluene solutions of purified sodium-butadiene rubber under conditions of possible isolation from the action of oxygen. The change of viscosity and molecular weight of a 4 per cent solution of rubber containing 6 per cent of disulfide during heating at 143° in sealed ampules of nitrogen is shown in Figure 2. The molec-

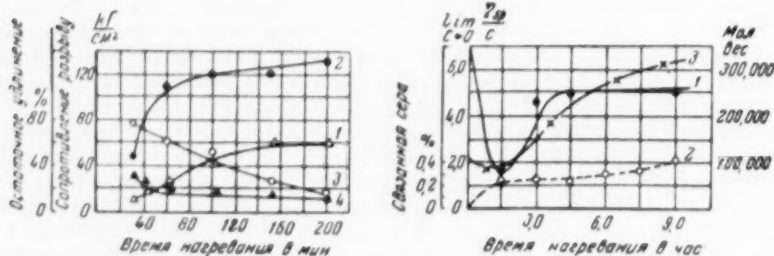


Fig. 1.—Change of tensile strength during heating of carbon-black mixtures of sodium-butadiene rubber: 1. Containing sulfur. 2. Benzothiazolyl disulfide. 3 and 4. Residual elongation. The abscissa indicates the time of heating in minutes; the left-hand scale of the ordinate the percentage residual elongation; the right-hand scale the tensile strength in kg. per sq. cm.

Fig. 2.—Change of (1) viscosity, (2) bound sulfur content, (3) molecular weight during heating of a solution of sodium-butadiene rubber with benzothiazolyl disulfide. The abscissa indicates the time of heating in hours; the left-hand ordinate the percentage bound sulfur; the middle ordinate the $\lim \eta_{sp}/c$; the right-hand ordinate the molecular weight.

ular weight was determined by light-scattering, as described by Dogadkin and Soboleva⁷. The observed change of the characteristic viscosity is typical of the vulcanization of rubber in solution: at first a decrease of viscosity is observed, due in part to heat destruction, and also to intramolecular combination of the rubber chains⁸ and the formation of isolated side-chain molecules. The effective volume of the dispersion phase in this case decreases; the viscosity of the solution also decreases. Later, when the individual molecules are united in larger spatial structures during the development of vulcanization, an increase of viscosity takes place. A direct indication of the combination of the molecules (structure formation or polymerization) can be seen in the increase of the molecular weight, which reaches three times its original value for crude rubber.

Similar phenomena were observed when the mixtures were heated in vulcanization presses. For this, the mixtures were prepared on micro-rollers mounted in a nitrogen chamber, so that all the operations of mixing and packing in vulcanization molds were carried out in an atmosphere of pure nitrogen in order to exclude the influence of oxygen during preparation and vulcanization⁹. All the ingredients were recrystallized and kept in nitrogen, and the rubber was cut out of the middle of a block immediately after removal from the polymerizer.

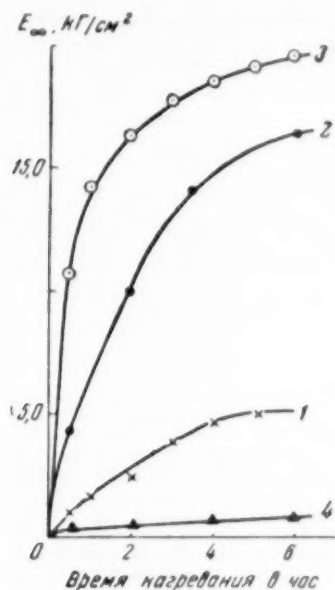


FIG. 3.—Change of equilibrium modulus of elasticity during heating of mixtures of: 1. Rubber and benzothiazolyl disulfide. 2. Rubber and sulfur. 3. Rubber, sulfur, and benzothiazolyl disulfide. The abscissa indicates the time of heating in hours; the abscissa E_{∞} in kg. per sq. cm.

Figure 3 shows the change of equilibrium modulus of elasticity E_{∞} during heating of a rubber (curve 4), a rubber mixture containing 6 per cent disulfide (curve 1), a mixture with 3 per cent of sulfur and 6 per cent disulfide (curve 2), and a mixture with 3 per cent sulfur and 6 per cent disulfide (curve 3). The modulus of elasticity E_{∞} was determined by a somewhat modified Meyer-Ferry method¹⁰. As is seen, heating a rubber at 143° does not cause any perceptible structure formation; the modulus is practically indeterminate and the rubber is completely soluble in xylene after heating for six hours. When a rubber mixture containing 6 per cent of benzothiazolyl disulfide is heated, a regular increase of the modulus E_{∞} to a value 5.1 kg. per sq. cm. is observed; the specimen is susceptible to only slight swelling in xylene (Table 1).

TABLE 1

CHANGE OF SWELLING MAXIMUM IN XYLENE (Q_M IN VOLUMETRIC RATIO) DURING HEATING AT 143° C OF RUBBER (A), RUBBER MIXTURE WITH 6 PER CENT BENZOTHAZOLYL DISULFIDE (B), MIXTURE WITH 3 PER CENT SULFUR (C), AND MIXTURE WITH 3 PER CENT OF SULFUR AND 6 PER CENT BENZOTHAZOLYL DISULFIDE (D)

Time of heating in hours	A	B	C	D
0.5		Solution	7.5	4.5
1		15.0	—	3.5
2		9.3	4.2	3.3
3	Saturated solution	7.4	—	3.0
4		6.6	3.6	2.9
5		6.3	—	2.9
6		6.0	3.4	2.8

According to contemporary theories of the nature of high elasticity, the equilibrium modulus depends on the number of chemical bonds between the molecular chains ($E_x = 3NkT$, where N is the number of segments between the nodes of the vulcanization structure). For this reason the existence of a final value of E_x and the increase of this value when the rubber mixture is heated with benzothiazolyl disulfide attests to the formation in this case of chemical cross-links characteristic of a vulcanizate.

The vulcanization process as observed by heating rubber with benzothiazolyl disulfide is accompanied by a change in the latter. Figure 4 shows an analysis of rubber solutions heated with benzothiazolyl disulfide¹¹. As is seen, ~50 per cent of the benzothiazolyl disulfide is changed; while part of it is converted into mercaptobenzothiazole (~25 per cent), the rest is absorbed in some form by the rubber, as was established according to the nitrogen and sulfur bond with the rubber.

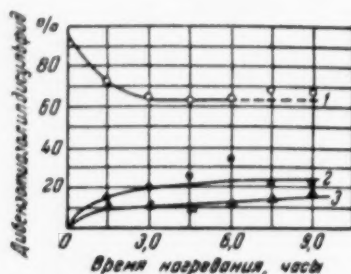


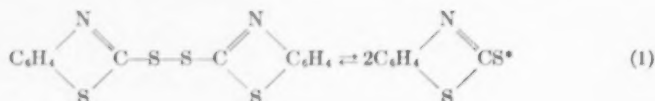
Fig. 4.—Change in content of: 1. Benzothiazolyl disulfide. 2. Mercaptobenzothiazole. 3. Sulfur, during heating of solution of sodium-butadiene rubber (in percentage of original benzothiazolyl disulfide content). The abscissa indicates the time of heating in hours; the ordinate the percentage of benzothiazolyl disulfide.

Similar data were obtained in analysis of mixtures heated in a press. In this case, however, the kinetic curve of formation of mercaptobenzothiazole has a maximum which coincides in time with the deflection of the curve of change of benzothiazolyl disulfide content.

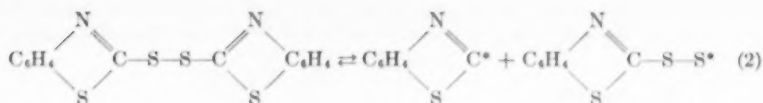
Parallel experiments showed that, if benzothiazolyl disulfide is heated in a solvent (xylene) in strict isolation from oxygen, no change takes place. Thus, the observed changes in benzothiazolyl disulfide during heating with rubber can be explained only by a chemical reaction between these substances. In particular, the conversion of benzothiazolyl disulfide into thiol can be regarded only as a consequence of a dehydrogenization process of separation of movable hydrogen from the α -methylene groups of the molecular chains of the rubber.

Comparing all the experimental data obtained, the following mechanism of reaction between benzothiazolyl disulfide and rubber, leading to vulcanization of the latter, can be proposed.

Under the conditions studied, reversible decomposition of benzothiazolyl disulfide into radicals takes place on heating, according to the following scheme:

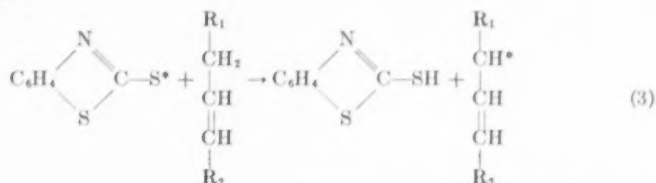


or

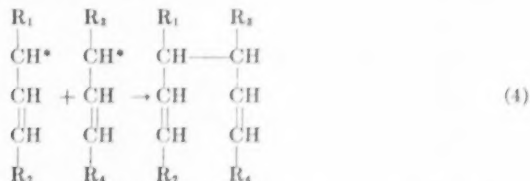


Further evidence of thermal decomposition into radicals is the fact that benzo-thiazolyl disulfide solutions at 120–150° are paramagnetic¹², while at 125° di-sulfide alone can cause polymerization of isoprene, as will be shown below. Symmetrical decomposition according to scheme (1) is more probable. This is confirmed by the fact that when radioactive benzo-thiazolyl disulfide, containing S³⁵ in the disulfide bridge, was used in a number of experiments, the activity of the sulfur in the vulcanizate and that which passes into the acetone extract was about the same. On the other hand, in one set of experiments, an unequal distribution of activities was observed (560 impulses per min. for the sulfur in the vulcanizate in contrast to 870 impulses per min. for that in the acetone extract); this makes it impossible to reject scheme (2).

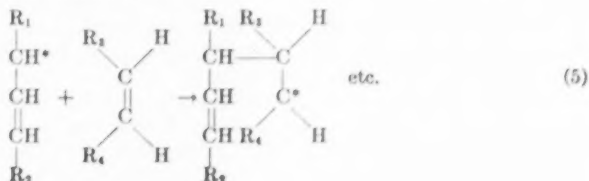
The radicals formed can react with the rubber molecules in two ways. The first reaction is between the radicals and the rubber molecules at the active α -methylene groups, accepting the mobile hydrogen atom; the energy of the bond of the latter with a carbon atom is weakened by a conjugation effect of approximately 19 kcal. per kg.-mol. Consequently the benzo-thiazolyl radical¹³ is converted into a molecule of mercaptobenzothiazole and a new polymer radical is formed:



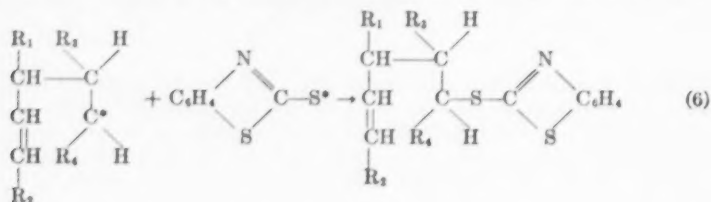
This latter can be recombined with the similar



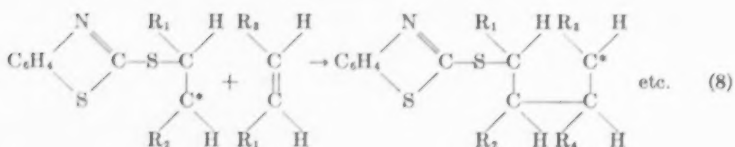
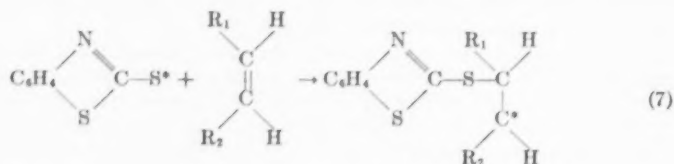
or react with a double bond of another rubber molecule, thus causing polymerization according to the scheme:



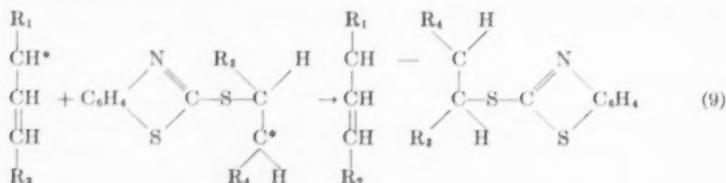
The process can be interrupted by any of several mechanisms, in particular as a result of the reaction of a polymer radical with a benzothiazolyl radical:



The second possible radical reaction is with the double bonds of the rubber molecules, which, in general, lead to a polymerization reaction, according to the scheme:



The reaction between polymer radical (1) and polymer radical (7) must be added to the indicated scheme.



As has already been mentioned, the development of process (3) is confirmed by the formation of mercaptobenzothiazole (see curve 2 in Figure 4). The possibility of reactions (6) and (7) is confirmed by the accumulation of bound sulfur and nitrogen in the rubber (see curve 3 in Figure 4), although our data do not indicate the presence of a bond of this accumulation with reaction (6) or (7), or with both reactions. The presence of sulfur and nitrogen in the rubber molecule in the form of a benzothiazolyl radical is confirmed by experiments on isotopic exchange in a vulcanizate prepared by heating with radioactive benzothiazolyl disulfide. The exchange is observed at 130° under conditions of diffusion of the crystalline inactive disulfide through a film of radioactive vulcanizate. The kinetics of exchange are shown in Figure 5; the maximum

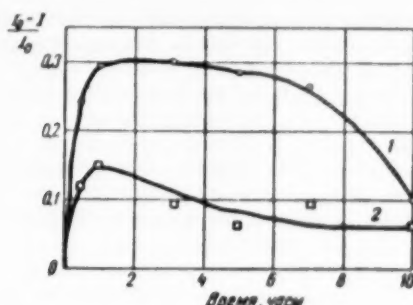
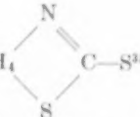
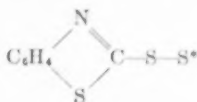


Fig. 5.—Kinetics of isotopic exchange between vulcanizate and benzothiazolyl disulfide (1) and sulfur (2). The abscissa indicates the time in hours.

on the curve shows that, besides the exchange between the C_6H_4  $\text{C}-\text{S}^{32}$ radicals present in the rubber molecule and the same inactive radicals, there is a further combination of benzothiazolyl radicals with the rubber. It is important to observe that a radioactive vulcanizate can also be exchanged with sulfur. This phenomenon can be easily explained if we assume the presence in a vulcanizate of a group characteristic of the disulfide radical:



The presence of $-\text{C}-\text{C}-$ bonds, which must be formed in the spatial structure of a vulcanizate because of the processes (4, 5, 8 and 9) is confirmed by

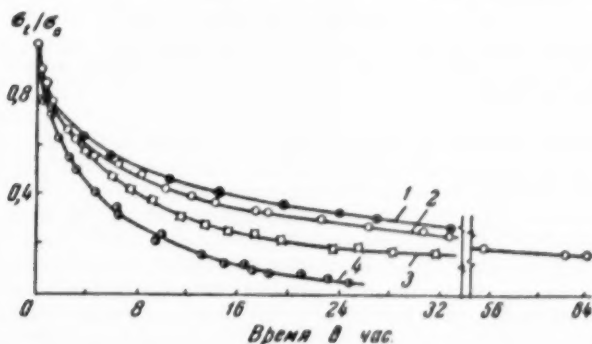


Fig. 6.—Stress relaxation in vulcanizates of synthetic rubber SK3-30 containing benzothiazolyl disulfide as vulcanizing agent and different amounts of sulfur. 1. 5 per cent benzothiazolyl disulfide; 2. 2 per cent benzothiazolyl disulfide and 0.5 per cent sulfur; 3. 2 per cent benzothiazolyl disulfide and 1 per cent sulfur; 4. 2 per cent benzothiazolyl disulfide and 2 per cent sulfur. The abscissa indicates the time in hours.

experiments on stress relaxation in vulcanizates at 130° in strict isolation from oxygen. The methods of these experiments and their importance in the analysis of vulcanization structures have been described earlier¹⁴. The kinetics of relaxation of vulcanizates prepared by heating with benzothiazolyl disulfide and sulfur are presented in Figure 6. As we have already shown¹⁴, the vulcanizates prepared with sulfur contain polysulfide $-S-S_x-S-$ bonds, which are thermally less stable than $-C-C-$ bonds. For this reason sulfur vulcanizates relax more rapidly (owing to thermal decomposition of the cross-links) and to a smaller relative equilibrium stress. The kinetic constant of relaxation of stress

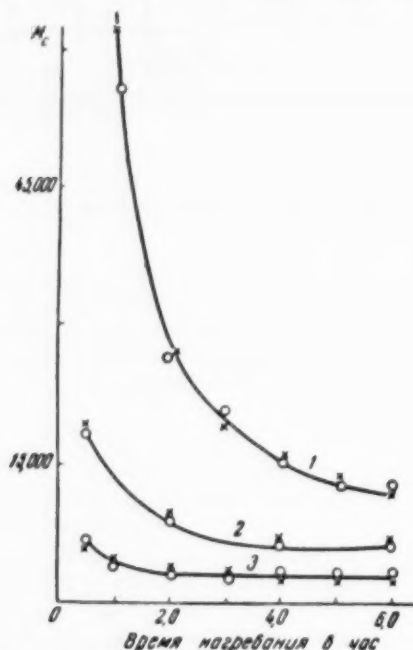


Fig. 7.—Change of molecular weight of M_c chain segments between unions of the spatial network of vulcanizate with heating, judged by swelling (crosses) and equilibrium modulus (circles). 1. Rubber-benzothiazolyl disulfide. 2. Rubber-sulfur. 3. Rubber-benzothiazolyl disulfide-sulfur. The abscissa indicates the time of heating in hours.

in vulcanizates prepared by heating with benzothiazolyl disulfide, calculated according to an equation of the first order at 130°, is $k = 4 \cdot 10^{-4} \text{ min.}^{-1}$, which indicates the presence in them of strong cross-links.

Inasmuch as the cross-links of a vulcanizate prepared by heating rubber with benzothiazolyl disulfide can be formed only as a result of polymerization reactions (4, 5, 8 and 9), it was interesting to determine the degree of development of these reactions. For this purpose it was necessary to measure the number of cross-links in a vulcanizate; this was done by two methods. The first method consisted in determining the maximum swelling of the vulcanizate in xylene and calculating the molecular weight M_c of chain segments according to the Flory-Rehner equation¹⁵. The second method consisted in determining the equilibrium modulus by the above-mentioned method and calculating M_c

by Wall's equation. The values of Mc obtained by the different methods were almost the same, as may be seen in Figure 7. This uniformity confirms the reliability of the obtained values of Mc and, consequently, the measured number of cross-links. The data from the calculations are given in Table 2.

Calculation of the number of linkages per benzothiazolyl radical, corresponding to the number of elementary acts of polymerization, involves certain difficulties. As has been observed above, mercaptobenzothiazole is formed during vulcanization, and combines with the rubber, however, without causing structure formation¹⁶. Naturally, then, it is necessary to subtract the equivalent of combined mercaptobenzothiazole from the total quantity of combined benzothiazolyl disulfide when measuring the amount of disulfide consumed in the formation of radicals which initiate the polymerization processes. The figures in Table 2, column 4, were obtained in this way. According to this calculation, 1.15-5.4 linkages are used by each disulfide molecule, and, consequently, each mercaptobenzothiazolyl radical requires 0.6 to 2.7 elementary acts of combination of the molecular chains of the rubber.

TABLE 2
CHANGE OF NUMBER OF —C—C— CROSS-LINKS FORMED DURING
HEATING OF RUBBER WITH 6 PER CENT BENZOTHIAZOLYL DISULFIDE

Time of heating in hours	Disulfide absorbed, in g. per cc. of rubber	Disulfide absorbed in form of mercaptobenzothiazole in g. per cc. of rubber	Disulfide absorbed in g.-mole/cc. of rubber $\times 10^4$ minus mercaptobenzothiazole in g.-mol./cc. of rubber $\times 10^{-14}$	Number of bonds per cc. of vulcanizate $\times 10^{-14}$	Number of bonds per molecule of absorbed disulfide
1	2	3	4	5	6
1	0.0122	0.0098	7.3	5.0	1.15
2	0.0199	0.0188	3.3	10.6	5.4
3	0.0281	0.0211	21.0	16.9	1.33
4	0.0267	0.0224	12.8	19.1	2.47
5	0.0264	0.0216	14.6	20.7	2.36

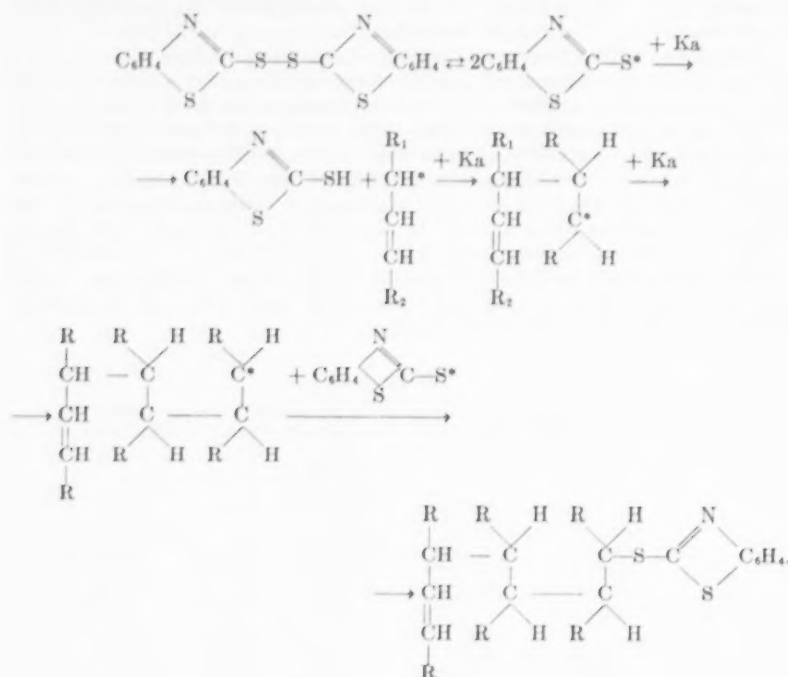
If the degree of cross-linking is determined from the inclination of the curve which describes the change in equilibrium modulus as related to the amount of reacting benzothiazolyl disulfide¹⁷, then 2.7 elementary acts for each benzothiazolyl radical are involved.

These values correspond closely to the direct measurement of the molecular weight of structured rubber after heating with benzothiazolyl disulfide (see Figure 2). As has been shown already, in this case the molecular weight increases as a result of vulcanization to three times its original value.

The calculations cited show that the development of polymerization chains initiated by benzothiazolyl radicals during vulcanization is very slight; on the average 2 acts of polymerization per radical are observed. This low value is explained by the fact that, after the first act of combination of two molecular chains (scheme 5 or 8), the active point of the new radical is already overloaded and has little mobility. Thus, further reaction of this radical will be possible as a result of either attraction of another molecular chain of rubber to it or a reaction with a mobile benzothiazolyl radical (scheme 6). In the latter case, rupture of the chain takes place¹⁸.

Proceeding from a given number of bonds and analytical data on the change

in benzothiazolyl disulfide, the vulcanization process described can be represented as following this scheme:



Inasmuch as these processes develop at various points on the molecular chains, all the molecular chains are interlaced to form a single spatial structure characteristic of the vulcanizate, despite the limited development of polymerization reactions. In the process described, the α -methylene groups play an important part, analogous to the views of Farmer¹⁹ on this phenomenon during rubber oxidation.

The capacity of benzothiazolyl radicals to cause polymerization was demonstrated by the authors in experiments on the polymerization of isoprene. For this purpose, isoprene in strict isolation from oxygen was heated at 125° in sealed ampules in the presence of a variable quantity of benzothiazolyl disulfide for 14 hours. The results are shown in Table 3.

TABLE 3

Disulfide content in percentage of isoprene	Reaction with isoprene		Yield of polymer in percentage
	in percentage of isoprene	in percentage of disulfide added	
0	—	—	22.0
0.45	0.43	87.5	24.1
2.20	1.99	93.1	33.5
2.46	2.00	80.7	27.8
3.70	2.51	69.7	32.8

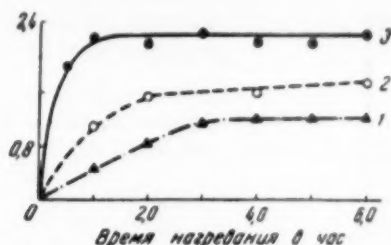
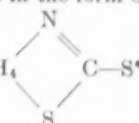


FIG. 8.—Kinetics of combination of sulfur according to vulcanization mixture: 1. Rubber-benzothiazolyl disulfide. 2. Rubber-sulfur. 3. Rubber-benzothiazolyl disulfide-sulfur. The abscissa indicates the time of heating in hours.

The product of polymerization is an oily liquid; this indicates a relatively low degree of polymerization. Most (up to 90 per cent) of the added disulfide was combined with the polymer. In no case was mercaptobenzothiazole detected. Thus, in this case the initiation of polymerization passed through a stage of combination of benzothiazolyl radicals with molecules of monomer.

In summation, we may assume that vulcanization under the influence of benzothiazolyl disulfide is a radical process of combination of molecular chains of the rubber, with the formation of —C—C— bonds. This process is initiated by benzothiazolyl radicals which are formed during heat dissociation of the disulfide, and the degree of development of polymerization of the chains is extremely slight: on the average two and not more than five elementary acts per initiating radical. The reaction of the benzothiazolyl radicals occurs principally in the α -methylene groups of the molecular chains of rubber, since, in the experiments described, about 50 per cent of the disulfide is converted into thiol and only about 20 per cent combines with the vulcanizate in the form of

groups which correspond to the benzothiazolyl radical C_6H_4 .

This radical enters the structure of the vulcanizate or is combined at a double bond or is combined with a polymer radical, thus causing rupture of the polymerization chain. Since the action of the benzothiazolyl radicals can take place at various points on the molecular chains, regardless of the small number of acts of polymerization, this process can lead to the formation of a spatial structure characteristic of the vulcanizate²⁰.

VULCANIZATION OF RUBBER BY SULFUR IN THE PRESENCE OF BENZOTHIAZOLYL DISULFIDE

Benzothiazolyl disulfide is one of the most widely used vulcanization accelerators. Its accelerating effect on the absorption of sulfur by rubber is seen in the curves of Figure 8, which show the results of heating mixtures of rubber containing 3 per cent of sulfur and rubber containing 3 per cent sulfur and 6 per cent benzothiazolyl disulfide under the conditions described above. In this case, as when rubber is heated with benzothiazolyl disulfide alone, a change in the latter is observed: a sharp decrease of the content of free disulfide in the first thirty minutes and partial conversion into mercaptobenzothiazole. Thus, the nature of the change in benzothiazolyl disulfide during sulfur vulcanization is

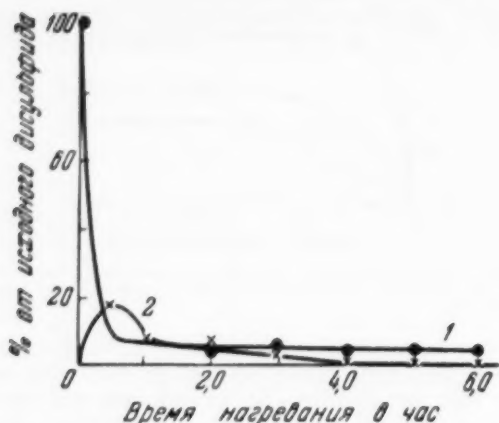


Fig. 9.—Change of contents. 1. Dibenzothiazolyl disulfide. 2. Mercaptobenzothiazole in acetone extract during heating of sodium-butadiene rubber with benzothiazolyl disulfide and sulfur. The abscissa indicates the time of heating in hours; the ordinate the initial percentage of disulfide.

the same as that observed when a rubber-disulfide mixture is heated. The difference is this: that the thiol formed later reacts with the ingredients of the vulcanized mixture, and is completely consumed by the end of the process. The maximum quantity of mercaptobenzothiazole formed is undoubtedly greater than that established experimentally and shown²¹ in Figure 9.

Absorption of fragments of accelerator by the rubber also takes place (Figure 10); this is due to the fact that the bound sulfur content is considerably

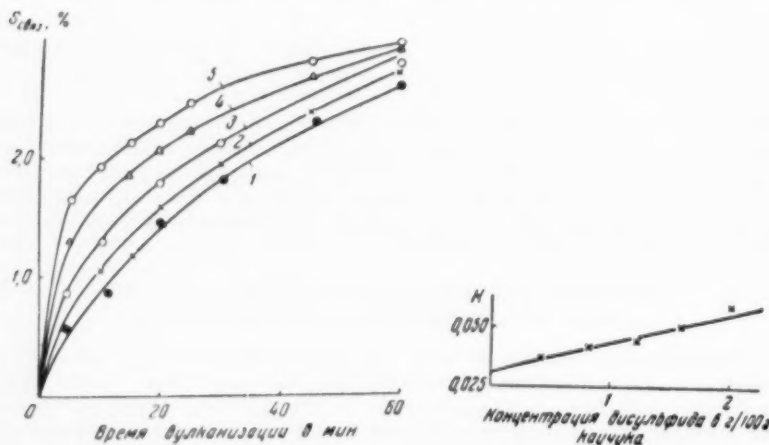


Fig. 10.—Kinetics of sulfur combination during vulcanization of a mixture of sodium-butadiene rubber in the presence of various concentrations of benzothiazolyl disulfide: 1. 0.4; 2. 0.8; 3. 1.2; 4. 1.6; 5. 2.0 per cent. The abscissa indicates the time of vulcanization in minutes; the ordinate the percentage bound sulfur.

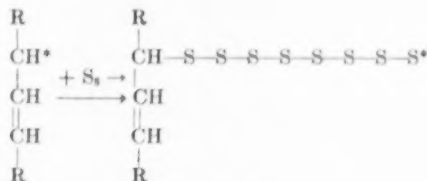
Fig. 11.—Relation between kinetic constants and concentration of accelerator. The abscissa indicates the concentration of disulfide in grams per 100 grams of rubber.

greater toward the end of the experiment than the quantity of sulfur added. The excess is carried away at the expense of combination with active disulfide molecules.

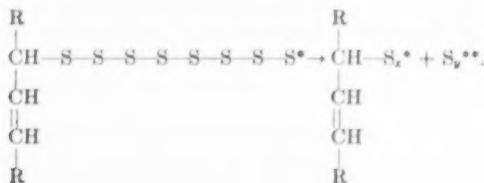
The kinetics of combination of sulfur with rubber in the presence of mercaptobenzothiazolyl disulfide is described by the equation of a monomolecular reaction. The kinetic constants increase linearly with an increase of the accelerator content (Figure 11).

This relation can be understood on the basis of the hypothesis that only half of the radicals which appear during the thermal decomposition of disulfides take part in the activation of sulfur. This agrees with the previous observation that about half of the disulfide is converted into a more active accelerator—mercaptobenzothiazole. The process of sulfur activation can have three possible courses:

(a) The eight-member S_8 ring reacts with the polymer radical formed according to reactions (3) and (7), resulting in the formation of a new polysulfide radical:



which can react further as such or, breaking off part of the sulfur atoms, in the form of biradicals with variable S_y^{**} content:

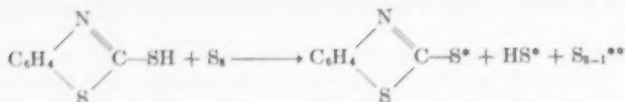


In summation, cross-bonds are formed, which absorb sulfur atoms.

(b) The eight-member S_8 ring reacts with a benzothiazolyl radical, forming intermediate (evidently polysulfide) compounds, which are decomposed, liberating sulfur biradicals S_y^{**} . The possibility of these reactions is confirmed by the property of isotopic exchange between benzothiazolyl disulfide and elemental sulfur²³ at vulcanization temperature²³. The new sulfur radicals S_y^{**} cause cross-linking of the molecular chains of the rubber.

(c) The eight-member S_8 rings react with mercaptobenzothiazole, which is formed in the initial stage of reaction (3). This reaction takes place according to either the mechanism of exchange reactions studied by Blokh²⁴ and Guryanova²⁵ or the mechanism of oxidation of mercaptobenzothiazole by elemental sulfur. The latter is being studied at present by the authors and I. Tutorskii. It has been established that, at vulcanization temperatures in an inert solvent,

hydrogen sulfide is liberated. Thus, the following reaction evidently occurs:



The essential moment is the opening of the eight-member sulfur ring, with formation of the S_p^{**} biradical, which is directly united to the rubber. The fate of the HS^* radical under vulcanization conditions varies. It may, by reacting with a mercaptobenzothiazole molecule or α -methylene group, form a hydrogen sulfide molecule. However, it is more plausible to suppose that it is combined

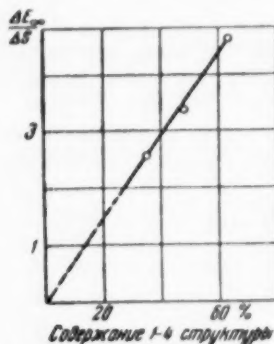


Fig. 12.—Relation between coefficient of bridge formation $\Delta E_{\infty} / \Delta S \approx \Delta n / \Delta S$ and content of 1,4-structure in rubber molecule. The abscissa indicates the percentage content of 1,4-structure.

with the double bond of a rubber molecule (Ka) and, consequently, takes part directly in the polymerization processes resulting from the formation of this radical:



In all the indicated schemes of consecutive and simultaneous reactions, the controlling reaction is the decomposition of disulfide into free radicals, since it requires the greatest activation energy. This reaction is by nature monomolecular. For this reason vulcanization, measured by the absorption of elemental sulfur, also follows an equation of the first order, as our data show.

Direct reactions between accelerator and rubber, described in the first section of this article, take place along with the sulfur process. As was shown, these processes lead to the formation of heat-stable cross-links $-\text{C}-\text{C}-$, while the reaction between rubber and S_p^{**} sulfur radicals leads to the formation of less stable polysulfide bonds. This is evident from the stress relaxation curves of vulcanizates (Figure 6) containing various proportions of accelerator and sulfur. The higher the proportion of accelerator, the more heat-stable is the vulcanizate, since a decrease in this ratio causes an increase of the proportion of polysulfide bonds in the vulcanizate.

It is also necessary to keep in mind that the α -methylene groups of the molecular chains of rubber also have an important part in sulfur vulcanization. This explains the striking fact that the relative change of the sulfur modulus

$\Delta E_{\infty}/\Delta S$ for butadiene polymers with various amounts of 1,2- and 1,4-structure increases linearly with an increase of double bonds in the main chains of the polymer (Figure 12). Thus, in sulfur vulcanization, accelerators such as disulfides and sulfenamides fill a double function by activating the sulfur and also activating the rubber itself. The latter effect has not been studied from a chemical standpoint. However, as was indicated above, this effect of accelerators is of essential importance to the mechanism of vulcanization.

CONCLUSIONS

1. Vulcanization of rubber by benzothiazolyl disulfide (without sulfur) is a radical process. The benzothiazolyl radicals formed during heat dissociation either are absorbed by a double bond or accept the mobile hydrogen of the α -methylene groups of the molecular chains of rubber. The polymer radicals formed thereby react with the other molecular chains, leading to combination of the molecules through the $-C-C-$ bonds into spatial formations characteristic of the vulcanizate.

2. Kinetic curves were obtained which describe the conversion of benzothiazolyl disulfide into mercaptobenzothiazole and combination with rubber molecules.

3. Changes of viscosity and molecular weight during the vulcanization of rubber solutions were studied by light-scattering. It was established that the kinetic curve of viscosity has a minimum, while the molecular weight increases to three times its original value toward the end of the process.

4. The number of $-C-C-$ cross-links in the vulcanizate was calculated from the swelling maximum and equilibrium modulus of elasticity. The data obtained indicate that, on the average, two and not more than five elementary acts of union of the molecular chains of rubber are necessary for each benzothiazolyl radical.

5. Experiments on stress relaxation at 130° established that the vulcanizate contains $-C-C-$ cross-links between the molecular chains of rubber.

6. The isotopic exchange of a radioactive vulcanizate with the diffused benzothiazolyl disulfide demonstrates the existence of benzothiazolyl groups in the structure of the rubber.

7. A scheme of the elementary radical reactions between rubber and benzothiazolyl disulfide which lead to vulcanization is given.

8. The kinetics of vulcanization of rubber with sulfur in the presence of benzothiazolyl disulfide was studied. The combination of sulfur follows a monomolecular law and the kinetic constant depends linearly on the concentration of accelerator.

9. In the earliest stage of sulfur vulcanization, benzothiazolyl disulfide is converted into mercaptobenzothiazole, which is consumed as vulcanization proceeds.

At the same time the rubber reacts with the benzothiazol radicals, which initiate polymerization processes with the formation of $-C-C-$ links between the molecular chains of rubber.

10. The ratio between $-C-C-$ bonds and sulfide bonds in a vulcanizate depends on the ratio between accelerator and sulfur.

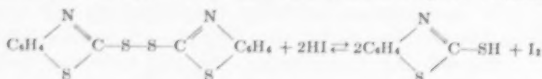
11. As in the case of vulcanization with benzothiazolyl disulfide, in sulfur vulcanization in the presence of an accelerator, the reactions involving the α -methylene groups of the molecular chains are of considerable importance in structure formation. Thus vulcanization can not be regarded as a process

which proceeds only at the double bonds of the rubber molecules. Activation of vulcanization by disulfides and sulfenamide accelerators is due to a large degree to reaction between these accelerators and the rubber.

12. A theory advanced in the present article together with experimental data reveal the radical mechanism of vulcanization and the action of accelerators, as well as the existence of polymerization phenomena during this process.

REFERENCES

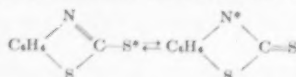
- ¹ Kainin, 1952 (no reference to publication, except year).
- ² Naylor, *J. Polymer Sci.* **1**, 305 (1946).
- ³ Fisher, *Ind. Eng. Chem.* **31**, 1381 (1939).
- ⁴ Dogadkin and Pevzner, *Izsladeniia po Khimii i Fizike Kauchuka i Reziny, Moskva, 1950*; Dogadkin, Smirnova, and Klauzen, *Trudy NTU Rezinschikov*, 1950.
- ⁵ Dogadkin, Feldshtein, and Dobromyslova, *Doklady Akad. Nauk S.S.S.R.* **92**, 61 (1953).
- ⁶ Zeide and Petrov, who studied the reaction of natural rubber with benzothiazolyl disulfide (*Kauchuk i Rezina*, 1937, No. 2, page 51) did not observe any vulcanization effect from this compound. Barton (*Ind. Eng. Chem.* **42**, 671 (1950)) reached the same conclusion.
- ⁷ Dogadkin and Soboleva, *Zhur. Fiz. Khim.* **26**, 72 (1952).
- ⁸ Zubov, Zhurkina, and Kargin, *Kolloid. Zhur.* **16**, 345 (1954); *RUBBER CHEM. AND TECHNOL.* **29**, 296 (1956).
- ⁹ The nitrogen chamber for obtaining rubber mixtures in an inert atmosphere was prepared in the Scientific Research Institute of the Tire Industry, according to a plan worked out by B. A. Dogadkin, V. B. Ezerskaya, and B. K. Karnin.
- ¹⁰ Meyer and Ferri, *Helv. chim. acta* **18**, 570 (1935).
- ¹¹ The stable benzothiazolyl disulfide was extracted with acetone and measured by the method of Kheraskova and Melamed by reducing potassium iodide in acetic acid according to the formula:



The mercaptobenzothiazole was measured by its reaction with copper oleate (Mogarycheva and Koretskaya, *Zhur. Rezinov. Prom.* **9**, 341 (1933)).

¹² Cutforth and Selwood, *J. Am. Chem. Soc.* **70**, 278 (1948).

¹³ This radical can evidently exist in two tautomeric forms (Moore, *Ind. Eng. Chem.* **11**, 4232 (1952)):



These radicals apparently take an equal part in the vulcanization process.

- ¹⁴ Dogadkin and Tarasova, *Doklady Akad. Nauk S.S.S.R.* **85**, 1099 (1952); *Kolloid. Zhur.* **15**, 348 (1953).
- ¹⁵ Flory and Rehner, *J. Chem. Physics* **11**, 521 (1943).
- ¹⁶ Barton, *Ind. Eng. Chem.* **42**, 671 (1950).
- ¹⁷ Bartenev, Dogadkin, and Novikova, *Kolloid. Zhur.* **10**, 94 (1948).
- ¹⁸ The limited nature of the process of polymerization makes the use of the term "combination" or "stitching" preferable. English-speaking authors call analogous processes "conjugate polymerization" (see Langlois, *Ind. Eng. Chem.* **45**, 1470 (1953)); however, Alfrey uses the term "polymerization" (see "Mechanical Properties of Polymers").
- ¹⁹ Farmer, *RUBBER CHEM. AND TECHNOL.* **16**, 17 (1943).
- ²⁰ Recently Scheele, Lorenz, and Dummer published a study (*Kautschuk u. Gummi* **8**, 29 (1955); *RUBBER CHEM. AND TECHNOL.* **29**, 15 (1956)) in which they propose a similar vulcanization mechanism for tetramethylthiuram disulfide. In this connection, it should be noted that a short work proposing a basic theory of the mechanism of vulcanization was published by the present authors in 1953 (Dogadkin, Shkurina, Dobromyslova, Feldshtein, and Kaplunov, *Doklady Akad. Nauk S.S.S.R.* **92**, 61 (1953)).
- ²¹ The formation of mercaptobenzothiazole during sulfur vulcanization with benzothiazolyl disulfide was observed by Zeide and Petrov (*Kauchuk i Rezina*, 1937, No. 2, p. 81), who explained this formation by the reaction between benzothiazolyl disulfide and hydrogen sulfide.
- ²² Guryanova and Vasil'yeva, *Zhur. Fiz. Khim.* **28**, 60 (1954).
- ²³ Recently we separated the tetrasulfide which is formed during the reaction between benzothiazolyl disulfide and sulfur during vulcanization.
- ²⁴ Blokh, Glubkova, and Miklukhin, *Doklady Akad. Nauk S.S.S.R.* **86**, 569 (1952).
- ²⁵ Guryanova, Syrkin, and Kuzina, *Doklady Akad. Nauk S.S.S.R.* **86**, 107 (1952).

THE VULCANIZATION OF BUTADIENE-STYRENE RUBBER IN THE PRESENCE OF SULFENAMIDE ACCELERATORS *

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In recent years, butadiene-styrene rubber has found a widespread and ever-increasing use in industry. This type of rubber, however, vulcanizes more slowly in industrial stocks than do natural and sodium-butadiene (polybutadiene) rubbers, and therefore it requires the use of powerful vulcanizing agents.

Among the several effective vulcanization accelerators for butadiene-styrene rubber are the sulfenamide compounds. For this reason, research on the vulcanization characteristics of butadiene-styrene rubber in the presence of these accelerators can no doubt be of considerable practical and theoretical interest.

The main substance under investigation in this work was *N,N*-diethyl-2-benzothiazolesulfenamide (Accelerator A-test). In order to establish whether or not a reaction takes place between the rubber and the *N,N*-diethyl-2-benzothiazolesulfenamide under the temperature conditions of vulcanization, research was carried out on both unloaded and loaded stocks (with channel black), some of which contained as their vulcanizing agent the accelerator alone, and others sulfur alone.

Figure 1 presents the kinetics of the change of the modulus at 300 per cent elongation during the heating of a stock containing 50 parts by weight of channel black and 5 parts of Rubrax per 100 parts of butadiene-styrene rubber, and of other stocks similar to this but containing also 3 parts of *N,N*-diethyl-2-benzothiazolesulfenamide in one case and 2 parts of sulfur in the other. Figure 1 shows that when a stock containing no curatives at all is heated (at the vulcanization temperature of 143° C), the modulus remains practically unchanged during all the time of heating. However, the introduction of 3 parts of *N,N*-diethyl-2-benzothiazolesulfenamide into such a stock has a definite vulcanizing effect. This is shown, in both the loaded and the unloaded stocks, by considerable increases of the modulus and tensile strength, the loss of plastic properties and a decrease of the swelling of the stocks. *N,N*-diethyl-2-benzothiazolesulfenamide in this case shows a considerably stronger structurizing (vulcanizing) action than does the usual vulcanizing agent, sulfur.

The character of the kinetics of the change (through heating) in the principal physico-mechanical and physico-chemical properties (especially the modulus, swelling, etc.) of stocks containing *N,N*-diethyl-2-benzothiazolesulfenamide is analogous to the changes of the properties of the usual sulfur stocks during vulcanization. In the latter case, the changes of the properties mentioned are brought about mainly by a chemical reaction between the vulcanizing agent, sulfur, and the rubber. However, in the presence of *N,N*-diethyl-2-benzothiazolesulfenamide, such a vulcanization mechanism cannot take place, since heating of this accelerator does not cause a liberation of elemental sulfur. At

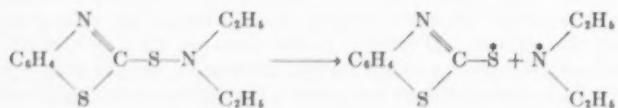
* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by Malcolm Anderson from the *Zhurnal Prikladnoi Khimii*, Vol. 28, No. 5, pages 533-542 (1955).

the same time it was established that the heated stocks with *N,N*-diethyl-2-benzothiazolesulfenamide contained chemically combined sulfur and nitrogen, which were not removed by prolonged extraction with acetone. This fact indicates the existence of a chemical reaction between rubber and the *N,N*-diethyl-2-benzothiazolesulfenamide under the temperature conditions of vulcanization. In Figure 2 are presented data characterizing the amounts of *N,N*-diethyl-2-benzothiazolesulfenamide which reacted, calculated as combined sulfur. As can be seen, a considerable portion of the accelerator introduced into the stock took part in the above reaction. Thus, when the stock was heated for 200 minutes at a temperature of 143° C, the quantity of reacted *N,N*-diethyl-2-benzothiazolesulfenamide reached 40 per cent of the amount introduced originally; it is important to note here that the physico-mechanical properties of the stock, as Figure 2 shows, also changed in accordance with the amount of *N,N*-diethyl-2-benzothiazolesulfenamide reacting. The relation between the modulus and the quantity of reacted *N,N*-diethyl-2-benzothiazolesulfenamide, in a heated stock, is represented (Figure 3) by a straight line. This is in agreement with the present-day idea that the modulus is a function of the number of cross-links between the molecular chains of the vulcanizate. The linear relation mentioned signifies that, in a given reaction, the number of acts of tying together rubber molecules is proportional to the number of molecules of *N,N*-diethyl-2-benzothiazolesulfenamide which have reacted with them.

However, the effect observed above might be explained to a certain extent by a reaction between the rubber and molecular oxygen which is activated by the presence of *N,N*-diethyl-2-benzothiazolesulfenamide. In order to eliminate this possibility, rubber stocks were prepared which contained only rubber and accelerator in one case, and rubber and sulfur in the other, and these were heated under conditions such that oxygen was excluded. Figure 4 presents data on the change of the solubility of these systems in chloroform, as a function of the duration of the heating. It is plain that in the system rubber-*N,N*-diethyl-2-benzothiazolesulfenamide, vulcanization takes place even in the absence of oxygen.

Thus the vulcanizing action of *N,N*-diethyl-2-benzothiazolesulfenamide is based on a direct chemical reaction between it and the rubber. The fact that such vulcanizates contain chemically combined sulfur and nitrogen indicates that these elements are able to enter into the molecular chains of the rubber in the form of radicals, which are produced from the *N,N*-diethyl-2-benzothiazolesulfenamide. From this, it is natural to suppose that vulcanization in the presence of *N,N*-diethyl-2-benzothiazolesulfenamide is related to the decomposition of such compounds into free radicals, which cause a polymerization of the rubber hydrocarbon. Such a vulcanization mechanism may be presented in the following form¹.

Under the temperature conditions for vulcanization, decomposition of *N,N*-diethyl-2-benzothiazolesulfenamide into radicals takes place, according to the reaction:



The action of such radicals may proceed in two directions.

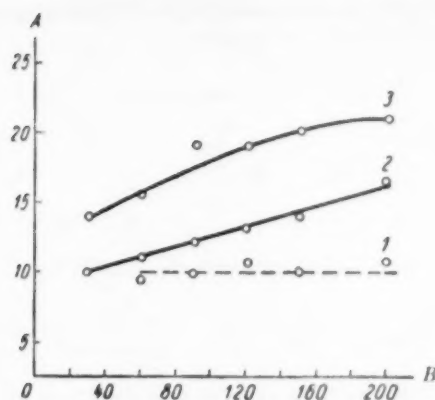
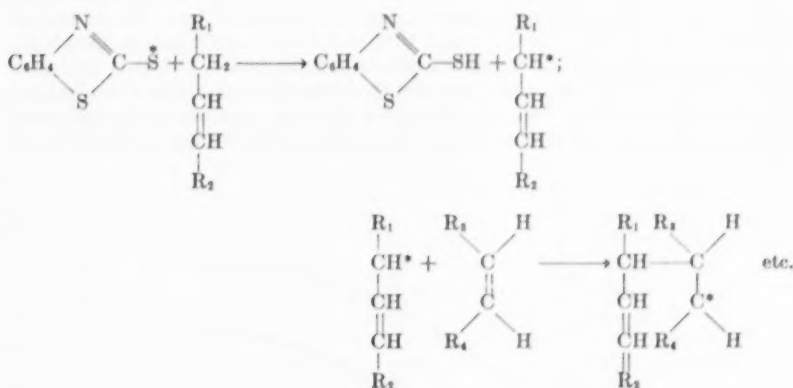


Fig. 1.—Kinetics of the change of modulus of stocks when heated at 143°C. 1.—100 parts by weight of SKS-30 and 50 parts of channel black. 2.—The same stock plus 2 parts of sulfur. 3.—The first stock plus 3 parts of *N,N*-diethyl-2-benzothiazolesulfenamide. The abscissa B represents the time of heating in minutes; the ordinate A the modulus at 300 per cent elongation, in kg. per sq. cm.

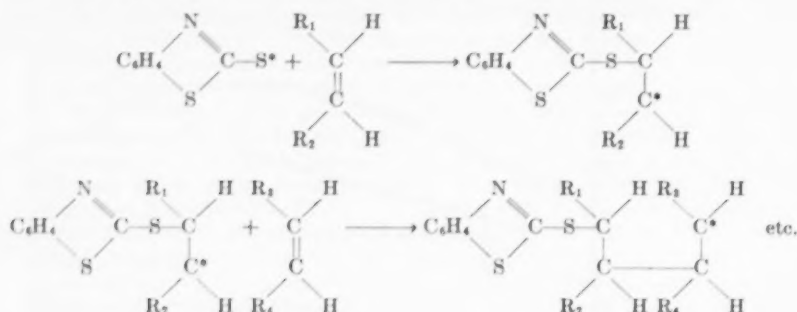
(1) They may accept hydrogen from the α -methylene groups of the molecular chains of the rubber, thus promoting the polymerization process according to the following reactions:



The 2-mercaptobenzothiazole formed is easily oxidized, by reaction with the rubber peroxides, to benzothiazolyl disulfide. The latter has actually been discovered in the vulcanization of stocks in the presence of *N,N*-diethyl-2-benzothiazolesulfenamide. We must also note that the presence of a phenyl ring in the structure of the butadiene-styrene polymer should favor the occurrence of the above reaction, since a phenyl ring increases the mobility of the hydrogen atoms² of the α -methylene groups in the molecular chains of the rubber.

(2) The radicals formed by the decomposition of *N,N*-diethyl-2-benzothiazolesulfenamide can react with the double bonds of the rubber molecule, pro-

moting a polymerization reaction according to the following equations:



The probability that such reactions occur is confirmed by the fact that the rubber combines with elements from *N,N*-diethyl-2-benzothiazolesulfenamide, and that the changes of the properties of the rubber during heating (vulcanization) is proportional to the consumption of this accelerator (Figure 3).

Undoubtedly the established fact of the structurizing (vulcanizing) action of *N,N*-diethyl-2-benzothiazolesulfenamide (Accelerator A-test) reveals the reason, or at least one of the reasons, why this type of accelerator is effective with respect to butadiene-styrene rubber, whose kinetics of combination with sulfur is comparatively slow.

The above phenomenon is of interest from the standpoint of clarifying the mechanism of vulcanization in general, and the nature of the action of the accelerator in particular. It is evident that in a sulfur vulcanization with *N,N*-diethyl-2-benzothiazolesulfenamide as the accelerator, not only does an exchange reaction with sulfur² take place, but also the radical polymerization mechanism discussed above occurs. One would expect that the existence of this polymerization in the presence of *N,N*-diethyl-2-benzothiazolesulfenamide would have a

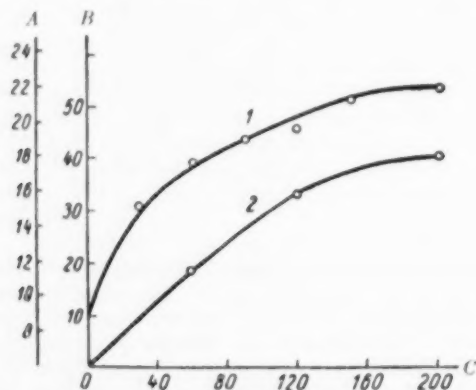


Fig. 2.—The amounts of *N,N*-diethyl-2-benzothiazolesulfenamide reacted in the stocks (Curve 2) and the change of modulus (Curve 1) as a function of the period of heating. The abscissa C represents the duration of the heating in minutes. Scale A of the ordinate represents the modulus at 300 per cent elongation, in kg. per sq. cm.; scale B the per cent of the *N,N*-diethyl-2-benzothiazolesulfenamide reacted.

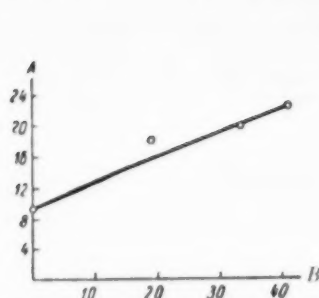


FIG. 3.—Relation between the modulus and the amount of *N,N*-diethyl-2-benzothiazole-sulfenamide reacted. The abscissa B represents the percentage of *N,N*-diethyl-2-benzothiazole-sulfenamide that has reacted; the ordinate A the modulus at 300 per cent elongation, in kg. per sq. cm.

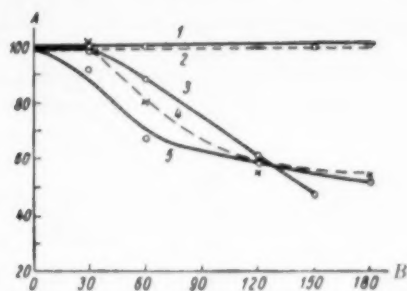


FIG. 4.—Change of solubility of butadiene-styrene rubbers containing *N,N*-diethyl-2-benzothiazole-sulfenamide when heated. 1.—SKS-30A heated in nitrogen. 2.—The same, heated in air. 3.—A stock containing 2 parts of sulfur per 100 parts of SKS-30A, heated in nitrogen. 4.—A stock containing 3 parts of *N,N*-diethyl-2-benzothiazole-sulfenamide per 100 parts of SKS-30A, in air. 5.—The same, in nitrogen. The abscissa B represents the time of heating in minutes; the ordinate A the solubility in chloroform, in percentage.

definite effect on the character of the vulcanization of sulfur stocks containing this accelerator, and on the properties of the vulcanizates obtained.

An investigation of the vulcanization of sulfur stocks was conducted with stocks containing two types of sulfenamide accelerators—*N,N*-diethyl-2-benzothiazolesulfenamide and *N*-cyclohexyl-2-benzothiazolesulfenamide. The activity of each of these accelerators was compared with that of an accelerator combination widely used at the present time; namely, diphenylguanidine plus benzothiazolyl disulfide.

Stocks were prepared which contained 100 parts by weight of the rubber, 50 parts of channel black, 5 parts of Rubrax, 5 parts of zinc oxide, 2 parts of stearic acid and 2 parts of sulfur; one set of these contained 0.75 part of diphenylguanidine and 0.6 part of benzothiazolyl disulfide, and the others equivalent amounts, in moles, of the sulfenamide accelerators. The kinetics of the change of the modulus of these stocks during the vulcanization process is presented in Figure 5. From the data obtained it is evident that, as regards the intensity of the vulcanization effect produced by equimolar quantities of accelerators (particularly as characterized by the physical and mechanical indexes of the vulcanizates), the sulfenamide compounds markedly exceeded in activity the combination of benzothiazolyl disulfide and diphenylguanidine used. That is, the former produced higher modulus and tensile strength values than the latter. Among the sulfenamide accelerators, further, *N*-cyclohexyl-2-benzothiazolesulfenamide caused a somewhat greater vulcanizing effect than did *N,N*-diethyl-2-benzothiazolesulfenamide.

The effectiveness of the sulfenamide accelerators is attested by the fact that when the concentration of these is increased, it is possible to reduce considerably the amounts of sulfur added. Not only can the sulfur content be lowered, but the accelerator activators zinc oxide and stearic acid can be eliminated from the vulcanizing compound altogether. Thus when a somewhat larger amount (1.5 to 2 parts by weight) of *N,N*-diethyl-2-benzothiazolesulfenamide is added to the usual rubber stocks (both the standard and the protector types), the sulfur content can be reduced considerably (by as much as 25 per cent) in the absence of accelerator activators. The vulcanizates produced thereby were

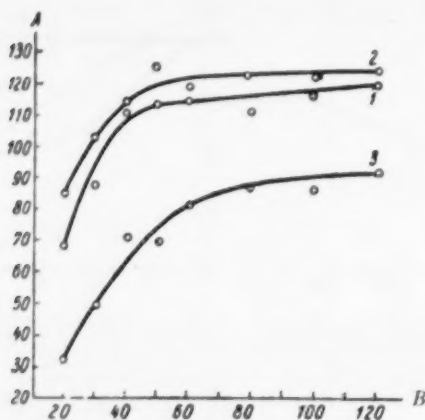


Fig. 5.—Change of modulus of stocks loaded with channel black. 1.—1.3 parts of *N,N*-diethyl-2-benzothiazolesulfenamide. 2.—1.45 parts of *N*-cyclohexyl-2-benzothiazolesulfenamide. 3.—0.6 part of benzothiazolyl disulfide and 0.75 part of diphenylguanidine. The abscissa B represents the time of vulcanization in minutes; the ordinate A the modulus at 300 per cent elongation, in kg. per sq. cm.

practically equivalent to the others in their physical and mechanical properties; but when the same amount of sulfur was used in these stocks as was used in the type of stocks having as their curatives diphenylguanidine, benzothiazolyl disulfide, zinc oxide and sulfur, then the sulfenamide stocks surpassed the latter in these properties.

In the light of the conception presented earlier as to the mechanism of the action of *N,N*-diethyl-2-benzothiazolesulfenamide, it is now understandable why the presence of this accelerator not only makes possible a reduction of the concentration of the vulcanizing agent, sulfur, but also compensates for the action of accelerator activators. Some data⁴ have been published recently from which one may presume that the presence of the activator zinc oxide, in a stock being vulcanized, has an oxidizing effect on the rubber thiols⁵ which are

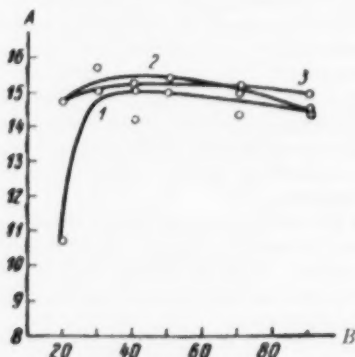
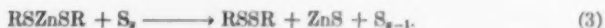
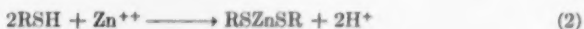
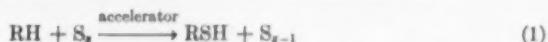
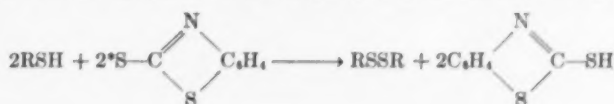


Fig. 6.—Change in the modulus of unloaded stocks. 1.—1 part of *N,N*-diethyl-2-benzothiazolesulfenamide. 2.—1 part of *N*-cyclohexyl-2-benzothiazolesulfenamide. 3.—0.5 part of benzothiazolyl disulfide and 1.0 part of diphenylguanidine. The abscissa B represents the time of vulcanization in minutes; the ordinate A the modulus at 400 per cent elongation, in kg. per sq. cm.

formed in the first stage of vulcanization. The supposition that the vulcanization of rubber proceeds through the formation of thiols is based on the fact that dithiols have proven to be effective vulcanizing agents. Thus, the production of a vulcanizate in such a case may be shown by the following reactions:



The oxidizing action of zinc oxide (Reaction 2) may, as is seen in the reaction scheme for *N,N*-diethyl-2-benzothiazolesulfenamide outlined above, be compensated for by the action of the radicals which are formed by the decomposition of this accelerator, and which accept hydrogen from the thiol groups:



Further, an increase of the concentration of *N,N*-diethyl-2-benzothiazolesulfenamide also makes it possible to eliminate accelerator activators from the stock.

In industrial practice, the composition of the curatives used (and in particular the accelerator content) is governed first of all by the commercial requirements of a given rubber stock. For this reason it was of importance to clarify the characteristics of the vulcanization kinetics of the accelerators studied, by employing them in concentrations such as to insure that the physical and mechanical indexes of the vulcanizates would agree relatively closely, where the time required to reach the optimum cure was the same in each. Naturally, for such a case the concentration of the mixture of diphenylguanidine and benzothiazolyl disulfide used had to be considerably greater, in moles, than the concentration of the sulfenamides. A study was made of some unloaded stocks, which differed from the loaded stocks considered above, not only in the accelerator content, but also in having 1.5 parts of sulfur instead of 2, and no carbon black or Rubrax. The results of determinations of their physical and mechanical properties showed that the quantities of the accelerators introduced were such as to insure that, when the optimum cure was reached, after 30 minutes, the vulcanizates produced would all have practically equal indexes. The 20-minute vulcanizates, however, differed from one another considerably. Thus, the vulcanizate from a stock containing *N,N*-diethyl-2-benzothiazolesulfenamide possessed lower modulus values (Figure 6) than did the 20-minute vulcanizates from the other stocks. However, to follow the kinetics of the process in its earlier stages by way of the physical and mechanical properties, under the usual test conditions, presents considerable difficulty. The vulcanization kinetics in the regions of 5, 10, 15, and 20 minutes and longer can be judged only by means of the data cited below for the combination of sulfur, the change of solubility and the change of the swelling limits.

The data presented in Figure 7 demonstrate that the sulfenamide accelerators produce a retardation in the kinetics of the sulfur combination reaction in its earlier stages (up to 15 minutes), in comparison with the benzothiazolyl disulfide-diphenylguanidine combination. The kinetic curve of vulcanization

in the presence of *N,N*-diethyl-2-benzothiazolesulfenamide has an S-shaped appearance, and clearly indicates that there is an induction period in the vulcanization. This period is lengthened considerably when the vulcanization temperature is lowered from 143° to 133° C.

While the sulfenamide accelerators cause a retardation of the vulcanization in its first stage, in the later stages they bring about an increase of the rate of the process, such that in 20 to 30 minutes (at a vulcanization temperature of 143° C) the combined sulfur content reaches its limiting value.

An analogous aspect of the vulcanization kinetics was shown by the data on the changes of the solubility of the stocks. Thus, after 5 minutes of vulcanization, the stocks containing *N,N*-diethyl-2-benzothiazolesulfenamide (Figure 8, Curve 1) were found to be completely soluble in chloroform, while those with a mixture of benzothiazolyl disulfide and diphenylguanidine exhibited a reduc-

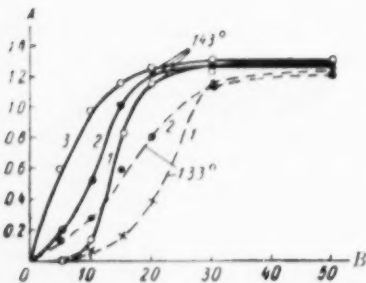


FIG. 7.—Kinetics of sulfur combination. 1.—1 part of *N,N*-diethyl-2-benzothiazolesulfenamide. 2.—1 part of *N*-cyclohexyl-2-benzothiazolesulfenamide. 3.—0.5 part of benzothiazolyl disulfide and 1 part of diphenylguanidine. Temperatures indicated are in degrees Centigrade. The abscissa B represents the vulcanization time in minutes; the ordinate A the per cent of combined sulfur.

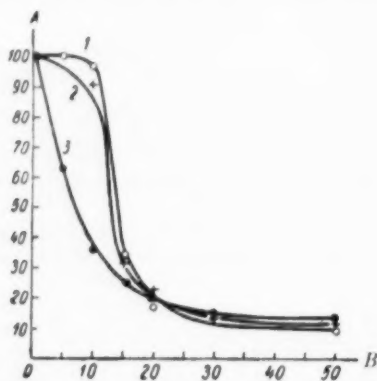


FIG. 8.—Change of solubility (chloroform extract) of stocks as a function of their periods of vulcanization. 1.—1 part of *N,N*-diethyl-2-benzothiazolesulfenamide. 2.—1 part of *N*-cyclohexyl-2-benzothiazolesulfenamide. 3.—0.5 part of benzothiazolyl disulfide and 1.0 part of diphenylguanidine. The abscissa B represents the time of vulcanization in minutes; the ordinate A the chloroform extract in percentage.

tion of almost 40 per cent of their solubility. In 10-minute vulcanizates of the latter, the reduction of solubility reached 64 per cent, against 4 to 10 per cent in vulcanizates containing sulfenamide accelerators. After 15 minutes of vulcanization, however, all these stocks had practically the same degree of solubility.

Of special interest, for showing up differences in the vulcanization kinetics of rubber stocks with sulfenamide accelerators, are the data from determinations of the equilibrium modulus. As Figure 9 shows, 10-minute and even 5-minute vulcanizates with *N*-cyclohexyl-2-benzothiazolesulfenamide are characterized by definite final modulus values, while in such vulcanizates with *N,N*-diethyl-2-benzothiazolesulfenamide, the equilibrium modulus equals zero. These data attest that in the presence of *N,N*-diethyl-2-benzothiazolesulfenamide the reaction of structuration, i.e., the creation of chemical bonds between the molecular chains of the rubber, did not quite bring about the forma-

TABLE I
SERVICE PROPERTIES OF VULCANIZED STOCKS OF THE TIRE-TREAD TYPE

Designation of indexes	0.5 part of Altax and 1 part of diphenyl- guanidine	1 part of <i>N,N</i> -di- ethyl-2- benzo- thiazole- sulfenamide	1 part of Santocure
Losses of mechanical properties at 20° C:			
(a) Coefficient of mechanical losses ($\sin \varphi$)	0.210	0.190	0.196
(b) Dynamic modulus E (in kg. per sq. cm.)	112	93	99
Heat build-up under dynamic compression at constant load (temperature of sample after 10,000 cycles, in ° C)	108	95	95
Resistance to dynamic deformation (in thousands of cycles):			
(a) Compression	16	21	22
(b) Flexure	135	180	180
Resistance to separation under dynamic shear (in cycles)	382	834	550

tion of a spatial vulcanizate structure in a 10-minute vulcanization of the stock at a temperature of 143° C.

The question naturally arises as to what effect such features of the vulcanization kinetics might have on the industrial properties of the rubber. An investigation of this question was carried out with stocks loaded with channel black and stocks of the protector type. The accelerator content of these stocks was such as to insure (for equal amounts of added sulfur) the production of vulcanizates all of which would be closely similar in their physical and mechanical indexes.

The above-noted characteristics of the vulcanization kinetics of unloaded stocks (depending on the different accelerators used) were noted also in loaded stocks; this was confirmed by determinations of combined sulfur on stocks of the protector type (Figure 10). Table I presents data characterizing some of the industrial properties of vulcanizates from stocks of the protector type. The data for heat-aging resistance, thermal stability, etc., are not included in the

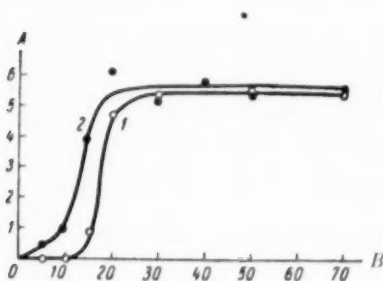


FIG. 9.—Change of equilibrium modulus of stocks containing *N,N*-diethyl-2-benzothiazolesulfenamide (1) and *N*-cyclohexyl-2-benzothiazolesulfenamide (2) during vulcanization. The abscissa B represents the time of vulcanization in minutes; the ordinate A the equilibrium modulus in kg. per sq. cm.

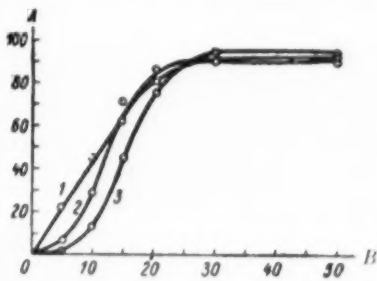


FIG. 10.—Kinetics of sulfur combination in loaded stocks of the tire-tread type. 1—0.5 part of benzothiazolyl disulfide and 1 part of diphenylguanidine. 2—1 part of *N*-cyclohexyl-2-benzothiazolesulfenamide. 3—1 part of *N,N*-diethyl-2-benzothiazolesulfenamide. The abscissa B represents the time of vulcanization in minutes; the ordinate A the percentage of the sulfur which has reacted.

table, since these indexes were identical in the stocks studied. The results given in the table show, however, a considerable difference in some properties between the sulfenamide vulcanizates and those obtained with the aid of benzothiazolyl disulfide and diphenylguanidine. The former exhibit less heat build-up than the latter, according to the data from temperature measurements during dynamic compression deformation and the data on losses in mechanical properties.

The vulcanizates containing *N,N*-diethyl-2-benzothiazolesulfenamide (Accelerator A-test) and *N*-cyclohexyl-2-benzothiazolesulfenamide (Santocure) are characterized also by a great resistance to dynamic compression and flexure deformation. It is this that makes the difference in service properties between the vulcanizates with *N,N*-diethyl-2-benzothiazolesulfenamide and those with *N*-cyclohexyl-2-benzothiazolesulfenamide; since, as the data in the table show, these vulcanizates are practically identical in all their properties other than those that characterize the strength of the adhesive bonds in a multilayer rub-

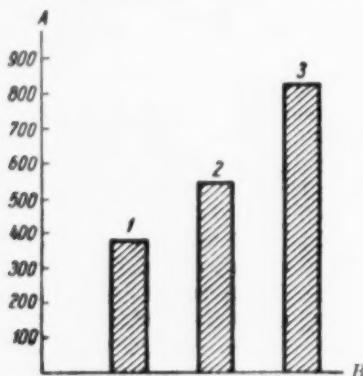


Fig. 11.—Strength of the bonds in plied stocks as a function of the type of accelerator used. 1.—Diphenylguanidine plus benzothiazolyl disulfide. 2.—*N*-Cyclohexyl-2-benzothiazolesulfenamide. 3.—*N,N*-diethyl-2-benzothiazolesulfenamide. The abscissa B represents the accelerator used; the ordinate A the resistance to separation under dynamic shear, in cycles.

ber stock. Thus, vulcanizates of stocks folded double, containing *N,N*-diethyl-2-benzothiazolesulfenamide, possessed a higher dynamic separation resistance (Figure 11) than did those containing *N*-cyclohexyl-2-benzothiazolesulfenamide. The latter, in turn, were considerably better than folded stocks containing benzothiazolyl disulfide plus diphenylguanidine. Thus, replacing the benzothiazolyl disulfide-diphenylguanidine accelerator group with *N,N*-diethyl-2-benzothiazolesulfenamide made the bonds between plies of folded vulcanizates twice as strong.

Such a positive effect by *N,N*-diethyl-2-benzothiazolesulfenamide on the strength of the bonds in folded stocks of butadiene-styrene rubber can be explained in the following way. As was established by the work of our laboratory, the strength of the bonds in cured folded butadiene-styrene rubber stocks depends to a considerable extent on how long these stocks remain in a semi-viscous condition. The existence of an induction period in the vulcanization of stocks with *N,N*-diethyl-2-benzothiazolesulfenamide, during which the folded stocks retain their fluidity, creates more favorable conditions for the raw rubber stock to spread and adhere to itself in the region of the fold; this causes an in-

crease in the strength of the adhesive bonds, in multilayer stocks. On the other hand, as was noted above, sulfenamide accelerators induce polymerization reactions involving the combination of molecular chains in the rubber. As a result of this, in vulcanizates with the sulfenamide accelerators we find not only sulfur bonds, but also the stronger —C—C— bonds present. The presence of the latter also imparts a higher strength to the bonds in folded stocks, as well as a higher fatigue resistance in vulcanizates of these. The —C—C— bonds created under the conditions stated are possibly more uniformly distributed throughout the spatial structure of the vulcanizate. This in turn has the effect of lowering the internal friction, and consequently of reducing the heat build-up, in the vulcanizates.

From the above presentation it is easy to understand why the use of sulfenamide accelerators gives rise to an improvement in several of the service properties of vulcanizates of butadiene-styrene rubber.

CONCLUSIONS

1. It is established that *N,N*-diethyl-2-benzothiazolesulfenamide has a structure-forming effect in stocks of butadiene-styrene rubber when these are heated at vulcanization temperatures, even in the absence of the usual vulcanizing agent, sulfur. These stocks, after extraction with acetone, still contain chemically combined sulfur and nitrogen, and the contents of these increase with a longer heating period.

2. The change of the modulus of the above stocks is a linear function of the amount of *N,N*-diethyl-2-benzothiazolesulfenamide which has reacted.

3. The structure-forming action of *N,N*-diethyl-2-benzothiazolesulfenamide can be regarded as a polymerization reaction, brought about by the free radicals formed in the thermal decomposition of this compound.

4. It is possible to vulcanize ordinary sulfur-containing butadiene-styrene rubber stocks in the presence of sulfenamide accelerators without the use of the accelerator activator, zinc oxide.

5. The kinetic curves of combination of sulfur and of the change of the equilibrium modulus, for ordinary sulfur stocks containing the sulfenamide accelerators (*N,N*-diethyl-2-benzothiazolesulfenamide and *N*-cyclohexyl-2-benzothiazolesulfenamide), is S-shaped, and shows an initial "induction" period in the vulcanization. This latter is especially distinct in stocks containing *N,N*-diethyl-2-benzothiazolesulfenamide.

6. Multilayer rubber articles made from plied stocks containing sulfenamide accelerators have stronger adhesive bonds. There are two reasons for this increased bond strength: (1) the retardation of the vulcanization kinetics in the initial stage of the vulcanization process, which is characteristic of the accelerators in question, and which has the effect of prolonging the length of time that the plied stocks remain in a semiviscous condition; and (2) the formation of the stronger —C—C— bonds as a result of polymerization reactions, which are stimulated by sulfenamide accelerators.

7. Vulcanizates prepared with sulfenamide accelerators are different from those with a combination of benzothiazolyl disulfide and diphenylguanidine in that the former have a lower heat build-up and a somewhat greater dynamic deformation resistance.

REFERENCES

- ¹ Dogadkin, Fel'dshteln, Dobromyslova, Shkurina and Kaplyunov, *Doklady Akad. Nauk SSSR* **92**, 1 (1953).
- ² Broun and Voronkov, *Zhur. Obshchei Khim.* **17**, 6, 1162 (1947).
- ³ Craig, Davidson and others, *RUBBER CHEM. & TECHNOL.* **24**, 2, 262 (1951).
- ⁴ Barton, *Ind. Eng. Chem.* **42**, 4, 671 (1950).
- ⁵ Bloomfield, *RUBBER CHEM. & TECHNOL.* **21**, 3, 543 (1948).

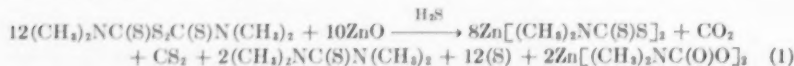
MECHANISM OF FORMATION OF ZINC DIMETHYLDITHIOCARBAMATE (ZnDMDC) IN TETRAMETHYLTHIURAM DISULFIDE (TMTD) VULCANIZATION *

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Scheele and Bielstein¹ recently have commented at length on the copolymerization (CP) theory of vulcanization which we proposed². They find the theory untenable with respect to TMTD vulcanization as well as with that using equivalent amounts of tetramethylthiuram monosulfide (TMTM) and sulfur. They feel that our presentation lacked in clarity and, therefore, that they did not understand it fully.

Scheele and coworkers report that 66 per cent of the TMTD, or of the mixture of equivalent amounts of TMTM and sulfur, reacts to form ZnDMDC according to the first-order rate law during vulcanization in the presence of excess zinc oxide. This finding is a notable contribution. In particular, it suggests the possibility of sulfur-oxygen interchange as a feature of the overall reaction, which we may write:



This reaction accounts for sulfur atoms needed for vulcanization and for the 66 per cent conversion of thiuram disulfide to zinc dithiocarbamate, but it omits the formation of TMTM, a compound that Scheele and Bielstein could not detect in any of their vulcanizates. In their work they used extraction with ethyl acetate, a technique that may be less elegant than shortpath distillation, which we used for isolating TMTM.

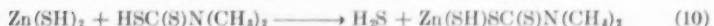
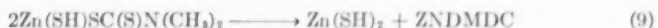
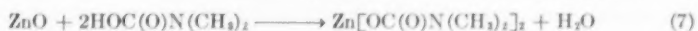
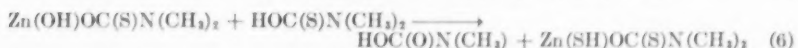
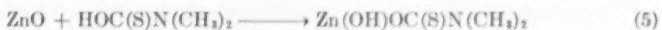
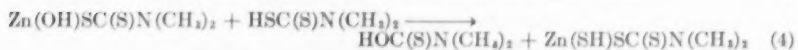
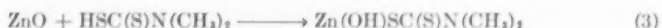
The formation of TMTM as an intermediate is an important feature of the CP theory as applied to TMTD vulcanization. TMTM reacts with sulfur in the absence of rubber at vulcanization temperatures to form TMTD, as shown by our studies³. As claimed by Scheele and Bielstein, this also is the result for these reactants in the presence of rubber and zinc oxide. Their data, however, show in rubber that the rate of formation of ZnDMDC above 120° is considerably faster from TMTM and sulfur than it is from TMTD. The two rates displayed the same temperature dependence above 120°. It is apparent, contrary to Scheele and Bielstein, that this kinetic proof does not apply to the formation of TMTD from TMTM and sulfur but to rubber-reactive intermediates. The rate studies indicate that TMTD forms similar intermediates to those formed from TMTM and sulfur, but, according to our vulcanization rate studies, TMTM and sulfur show an induction period and, as is well known, TMTM was the first delayed-action accelerator worthy of note. When vulcanization sets

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in, however, the rate of vulcanization is considerably faster than it is in the case of TMTD vulcanization.

The data of Scheele and Bielstein show that there is no induction period in the formation of ZnDMDC from TMTM and sulfur in rubber. This indicates among other things that ZnDMDC formation and vulcanization are not necessarily related directly.

Our study of TMTD vulcanization shows⁴ that more TMTM is present during the early stages than during the later stages. Its disappearance can be the result of the formation of carbon disulfide and tetramethylthiourea (TMTU), for which, in the absence of rubber and zinc oxide, catalytic amounts of hydrogen sulfide or dimethylamine suffice. With zinc oxide present, mixed salts of zinc hydrosulfide and zinc hydroxide can be expected. Of these, zinc hydroxide dimethyldithiocarbamate is the most obvious. Reactions (2) through (10) summarize our formulation for the way TMTM disappears during TMTD vulcanization.



It may be recalled that our early work³ showed that TMTD and zinc oxide react⁵ to form ZnDMDC, sulfur, carbon disulfide, and carbon dioxide. Actually, in the experiment reported on, the yields of sulfur and ZnDMDC isolated were 52 and 67.5 per cent, respectively. These data and those of Scheele and coworkers constitute good evidence that ZnDMDC is formed mainly by a sulfur-oxygen interchange reaction and not by a stoichiometric dehydrogenation reaction.

We hope to report more fully at a later time on the chemistry of TMTD.

REFERENCES

- ¹ Scheele and Bielstein, *Kautschuk u. Gummi* **8**, 251 (1955); *RUBBER CHEM. AND TECHNOL.* **29**, 49 (1955).
- ² Craig, Juve, Seimon, Davidson, and Hay, *J. Polymer Sci.* **8**, 321 (1952); *RUBBER CHEM. AND TECHNOL.* **26**, 57 (1953).
- ³ Craig, Davidson, Juve, and Geib, *J. Polymer Sci.* **6**, 1 (1951); *RUBBER CHEM. AND TECHNOL.* **24**, 262 (1951).
- ⁴ Craig, Davidson, and Juve, *J. Polymer Sci.* **6**, 177 (1951); *RUBBER CHEM. AND TECHNOL.* **24**, 275 (1951).
- ⁵ Jarrigon, *Rev. gén. caoutchouc* **20**, 155; 177 (1943); *RUBBER CHEM. AND TECHNOL.* **19**, 1061 (1946).

A STUDY, BY MEANS OF RADIOACTIVE SULFUR, OF THE MECHANISM OF VULCANIZATION OF RUBBER. I *

S. E. BRESLER, V. I. PRYADILOVA, AND V. YA. KHAJMAN

INTRODUCTION

The vulcanization of rubber and conversion into a cured product is a very old and important process in rubber technology. An enormous literature has been devoted to the study of the vulcanization process. However, the bulk of this work consists of purely technological investigations, which do not contribute to the clarification of the inner causes of the phenomena observed.

The present-day view of vulcanization is that it involves the formation of short chemical bridges between linear macromolecules of rubber. According to the usual theory, these bridges can be formed as a result of the combining of one or several atoms of sulfur at the double bonds in the rubber.

The existence of the bridges converts the polymer from a plastic to an elastic substance, and makes it insoluble in organic solvents, although capable of limited swelling.

It is easy to see the limitations and inadequacies of these concepts. In the first place, it is not clear what is the special position of sulfur among the varied vulcanizing agents. It is known that oxygen, too, has the ability to tie together macromolecules of the rubber at their double bonds. In synthetic rubbers it is possible for bridges to be formed between the chains through the creation of C—C bonds; i.e., by further polymerization.

However, none of the other vulcanizing agents can compare with sulfur with respect to the quality of the resulting products. Because of this, we are convinced that the presence of bridges, in itself, is not sufficient to give the characteristics of vulcanization. Just any sort of bridge whatever is not suitable in practice. Sulfur, in this respect, has an indisputable advantage. This fact requires explanation.

A second important question concerns the so-called combined and free sulfur. In most of the work, the free sulfur was removed from the vulcanizate by a solvent (acetone or carbon disulfide). Much and varied speculation has arisen about the sulfur which remains in the rubber. Sometimes this has been considered to be simply diffused amorphous sulfur (S_μ), which is insoluble in organic solvents. There is not much basis for such conclusions. The solubility of sulfur in rubber is such that the amount of it used in vulcanization (about 2 per cent) is present in the form of a true molecular solution.

If we consider all combined sulfur to be chemically bound to the rubber, the question naturally arises—how is it bound? The creation of bridges, at first glance, would seem to require only a little sulfur. And, in fact, it has been shown that it is possible to produce vulcanizates containing as little as 0.15 per cent total sulfur¹. It is hard to reconcile this with the fact that, in a cured stock, the quantity of combined sulfur is 10 to 20 times greater than this.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by Malcolm Anderson from the *Zhurnal Tekhnicheskoi Fiziki*, Vol. 24, No. 4, pages 577-598 (1954).

The third question concerns the kinetics of vulcanization. The following remarkable fact has been observed: the rate of combination of sulfur with rubber remains constant during all the time of vulcanization until most of the sulfur has been consumed. This means that the rate of sulfur combination depends, not on the free sulfur concentration, but on the concentration of total sulfur, i.e., on the sum of the free and combined sulfur². This fact cannot be explained away by any such trivial reasons as, for instance, the processes of solution and diffusion of elemental sulfur.

Among the facts which are not compatible with a simple concept of vulcanization as a process of tying chains together with sulfur atoms, is that of the behavior of ebonite—a rubber vulcanized to the limit, with a sulfur content of 32 per cent. The literature is full of attempts to present ebonite as a definite stoichiometric compound of the hydrocarbon with sulfur, with a composition of, let us say, $(C_6H_8S)_n$.

There are no conclusive data whatever for this. On the contrary, a determination of the number of double bonds, from the characteristic absorption band in the infrared region (about 6 microns), shows that ebonite still retains a considerable portion of the double bonds of the rubber³.

If one assumes that ebonite, a spatial polymer combined to the maximum degree with sulfur, in which the energy of the bridge bond is that of the chemical bond C—S (or 54,000 cal./mole)⁴, then it is hard to understand just how it softens at 80° C and changes into an elastic state, with a low modulus of elasticity.

We may note that in a rubber whose chains are tied together with C—C chemical bonds, such a change is not observed. Another fact related to this is that, at 100° C, a vulcanizate can be entirely dissolved in a solvent, e.g., in toluene containing piperidine; and if the polymer is then precipitated from the solution, the precipitated substance is found to have the properties of the vulcanizate again⁵. To be sure, our concepts of the chemical nature of vulcanization have varied somewhat. But, at the same time, it is known that all attempts to interpret vulcanization as a purely physical phenomenon have proven entirely fruitless and have been abandoned.

The present work has been carried out as an attempt at a quantitative study of the vulcanization process at different stages. The method of labeled atoms seemed a very suitable one to employ for this purpose.

We measured, over a wide range of temperatures, the solubility and the diffusion coefficient of sulfur in natural rubber, and we also studied the kinetics of the combination of sulfur with rubber in the presence of accelerators. Besides this, we investigated the reaction of isotope exchange between the accelerator and the sulfur, and were thus able to interpret the role of the accelerator.

THE DIFFUSION OF SULFUR IN RUBBER AND THE SOLUBILITY OF SULFUR

It was logical that our thoughts should turn to a study of rubber vulcanization by means of research on migration, i.e., the diffusion of sulfur in the rubber. The very concepts of combined sulfur and free sulfur presuppose a lack of migration in the case of the former, and an ability to diffuse on the part of the latter.

It would seem that, taking diffusion as the index, one might investigate the kinetics of the combination of sulfur with rubber successfully in a considerably

simpler manner, and in a much broader range of temperatures and concentrations, than would be possible by chemical, i.e., extraction, methods.

The available data on the diffusion of sulfur in rubber are very scanty⁶. The use of radioactive sulfur makes possible measurements of diffusion very quickly and accurately, and at practically any temperatures.

THE PROCEDURE FOR THE DIFFUSION EXPERIMENTS

Figure 1 shows the apparatus with which the measurements of sulfur diffusion in rubber were carried out. Natural rubber was milled into sheets of various thicknesses of 0.5 to 2 mm. This variation in thickness was intentional, so as to check the accuracy of the data obtained. On the bottom side of the rubber sheet 2 was placed a small quantity of radioactive sulfur (of the order of 0.01-

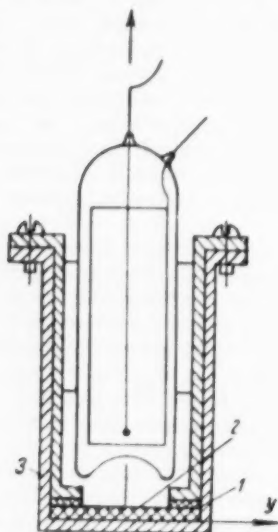


FIG. 1.—(No caption given; this is the apparatus for radioactivity measurements.)

0.02 per cent by weight of the rubber), with a total radioactivity of the order of 0.1 microcurie. Above this was placed a Geiger counter, which registered the β -particles of that sulfur which succeeded in migrating through the sheet. Since sulfur S^{35} emits β -particles whose spectrum limit is at 170 kev, these are capable of penetrating only a thin layer of material. The thickness of a rubber layer from which the counter could "see" a particle of S^{35} was 30 microns, according to our measurements (see below).

The diffusion coefficient of sulfur in rubber was determined according to the relation between radioactivity, as registered by the counter, and time.

The apparatus consisted of the brass cylinder 3. On the bottom of this cylinder was placed a sample of rubber 2. On both sides of the sample were applied sheets of mica 10 microns thick, which prevented the sulfur from escaping in the diffusion process from the surface of the sample.

A brass plate was pressed on top of the sample. Opposite a hole in this plate was placed a special all-glass end-window Geiger counter (the thickness of the

window being 15 microns), with which measurements could be made at temperatures up to 200° C. The counter was centered in the apparatus with the aid of a cylindrical sleeve.

The apparatus, assembled in this manner, was immersed in a constant-temperature oil bath, and the time was counted from this moment. The control experiments showed that the temperature of the sample was governed by the time, which was less than 5 minutes. During the heating, the radioactive sulfur, which had been put on the bottom surface of the sample, diffused through it. The counter measured the concentration of sulfur in the vicinity of the top surface of the sample.

The experimental data make it possible (1) to judge how accurately the diffusion process is described by the equation: $\partial u / \partial t = D(\partial^2 u / \partial x^2)$; (2) to determine the diffusion coefficient of sulfur in rubber at various temperatures; and (3) to calculate the activation energy for the diffusion of sulfur in rubber.

PROCESSING OF THE EXPERIMENTAL DATA AND THE RESULTS

In the absence of vulcanization accelerators, sulfur reacted slowly with the rubber, and the concentration of the sulfur had become uniform throughout in the period of the experiment (of the order of 1 hour) before any appreciable part of the sulfur had combined with the rubber. In this case one would logically expect that the course of the process could be described by a diffusion equation.

We can use the equation for one-way diffusion: $\partial u / \partial t = D(\partial^2 u / \partial x^2)$, where $u(t, x)$ is the concentration of sulfur at the moment in time t on the x -coordinates, since the diameter of the sample (30 mm.) is many times greater than its thickness (about 1 mm.).

Thanks to the mica sheet, the flow of sulfur through the surface of the sample was nil. (The radioactivity of the mica sheets themselves, determined after the experiment was completed, appeared to be negligible.)

At the initial moment of time, all the sulfur was located on the bottom surface of the sample.

If we line up the x -axis along the axis of the apparatus (Figure 1), and superimpose the coordinates at the beginning on the bottom surface of the sample, then the boundary and initial conditions will take the following form:

$$\left. \frac{\partial u}{\partial x} \right|_{x=0} = \left. \frac{\partial u}{\partial x} \right|_{x=d} = 0, \quad u \Big|_{t=0} = u_0 \delta(x)$$

where $u(x, t)$ is the concentration of sulfur; D is the diffusion coefficient; d is the thickness of the sample; u_0 is the quantity of sulfur put on the sample; $\delta(x)$ is the delta-function, equal to ∞ where $x = 0$ and equal to zero for all other points in space; as we know,

$$\int_0^\infty \delta(x) dx = 1.$$

The concentration of sulfur on the top surface of the sample in this case can be expressed in the form of the series:

$$u(t, d) = u_0 + 2u_0 \sum_{n=1}^{\infty} e^{-\left(\frac{\pi n}{d}\right)^2 Dt} (-1)^n. \quad (1)$$

This series quickly converges at "large" periods of time in the experiment, and under the condition $(\pi/d)^2 Dt > 1.5$, the value of the series can be limited to the first member with an error of less than 1 per cent. Assuming that the measured radioactivity is proportional to the concentration of sulfur at the surface, we get a working equation:

$$I(t, d) = I_\infty - 2I_\infty e^{-\left(\frac{\pi}{d}\right)^2 Dt} \quad (2)$$

where $I(t, d)$ is the radioactivity measured by the counter at the surface $x = d$; I_∞ is the radioactivity measured at the surface after the sulfur concentration became uniform. If we let the abscissa axis represent time and the ordinate the quantity $-\ln[1 - (I/I_\infty)]$, then, according to Equation (2), the experimental points should lie on a straight line, the extension of which intersects a segment of the ordinate which is equal to $-\ln 2$. This makes it possible to ascertain whether or not the process is described accurately by the equation: $\partial u / \partial t = D(\partial^2 u / \partial x^2)$.

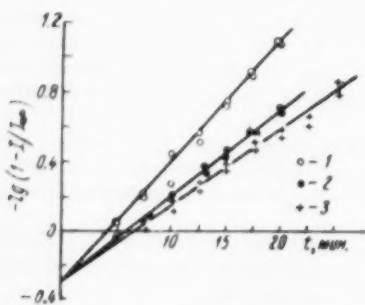


FIG. 2.—1— $t = 126^\circ \text{C}$. 2— $t = 111^\circ$. 3— $t = 106^\circ$. The points were obtained from two experiments. The abscissa represents the time in minutes; the ordinate represents $-\log(1 - I/I_\infty)$.

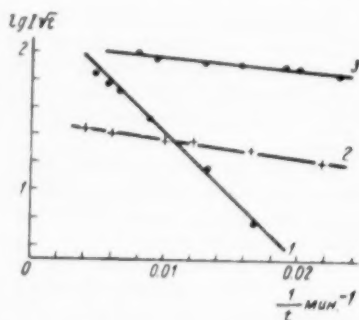


FIG. 3.—1— $d = 0.38 \text{ mm}$; $D = 2.05 \times 10^{-7} \text{ sq. cm./sec.}$. 2— $d = 1.06 \text{ mm}$; $D = 2.18 \times 10^{-7} \text{ sq. cm./sec.}$. 3— $d = 0.28 \text{ mm}$; $D = 1.94 \times 10^{-7} \text{ sq. cm./sec.}$ The abscissa represents $1/t$ ($t = \text{time in minutes}$); the ordinate $\lg I \sqrt{t}$.

From the experimental straight lines, the coefficient of diffusion was determined, since the tangent of the straight line's angle of slope is equal to $(\pi/d)^2 D$.

Figure 2 shows a series of such experimental straight lines. Changes in the sample thickness and in the temperature do not affect the linear relationship nor the initial position on the ordinate.

For processing the data of experiments conducted at high temperatures, the solution given above was adequate; but for those of experiments at low temperatures, where the diffusion process proceeded slowly, it was expedient to use a solution in a different form, which gave a series converging rapidly at short periods of diffusion time. This solution can be derived easily, and takes the form:

$$u(t, d) = \frac{u_0}{\sqrt{\pi Dt}} \sum_{n=1}^{\infty} e^{-\frac{(2n-1)^2 \pi^2 D}{4Dt}} \quad (3)$$

Under the condition $d^2/4Dt > 1.5$, the value of the series can be limited to the first member, with an error of less than 1 per cent. Assuming that the

measured radioactivity was proportional to the sulfur concentration at the surface $x = d$, we derived a working equation:

$$I(t, d) = \frac{I_0}{\sqrt{\pi Dt}} \cdot e^{-\frac{d^2}{4Dt}}$$

Letting the abscissa represent the quantity $1/t$ and the ordinate $\log I\sqrt{t}$, we got a straight line, the tangent of whose angle of slope determined the diffusion coefficient. A series of experimental straight lines obtained by this method are presented in Figure 3.

TABLE I

Method of calculation	$d(\text{mm.})$	$T(^{\circ}\text{C})$	$D \times 10^4$ ($\text{cm.}^2/\text{sec.}$)
$\ln I\sqrt{t} = A - \frac{d^2}{4Dt}$	0.28	50	0.194
	0.38	50	0.205
	1.06	50	0.218
	0.36	73	0.44
$\ln\left(1 - \frac{I}{I_{\infty}}\right) = \ln 1.27 - \left(\frac{\pi}{2d}\right)^2 Dt$	1.03	73	0.40
	0.34	100	0.77
In the presence of accelerators—	0.53	140	2.20
$\ln\left(1 - \frac{I}{I_{\infty}}\right) = \ln 2 - \left(\frac{\pi}{d}\right)^2 Dt$	0.90	140	2.26
	0.80	125	1.61

In cases where large amounts of sulfur were placed on the sample, the diffusion coefficient was calculated by the use of a solution of the diffusion equation under the boundary conditions:

$$u_{x=0} = u_0 \quad \text{and} \quad \frac{\partial u}{\partial x} \bigg|_{x=d} = 0.$$

This boundary condition implies that we have, on the bottom surface of the sample, at all times a constant concentration of sulfur, which is equal to the amount of saturation.

A working equation for this case under the condition of "large" periods of time would take the form:

$$I(t, d) = I_0 - 1.27 I_0 e^{-\left(\frac{\pi}{2d}\right)^2 Dt}.$$

The values for the diffusion coefficient, which were derived from experiments with samples of different thicknesses and calculated through various equations, agree with one another, and agree likewise with the diffusion coefficient of sulfur in the presence of accelerators. The absolute values of the diffusion coefficients at temperatures of 130–150° C are of the order of 10^{-6} $\text{cm.}^2/\text{sec.}$; i.e., they are typical of the diffusion of small molecules in a viscous liquid.

The results of diffusion measurements made at various temperatures and thicknesses of samples, and calculated with various equations, are presented in Table I. Figure 4 shows a graph of the quantity: $\log D = f(1/T)$.

We are convinced that the rule: $D = D_0 e^{-u/RT}$, agrees satisfactorily with experiment, and the activation energy for diffusion proved to be equal to

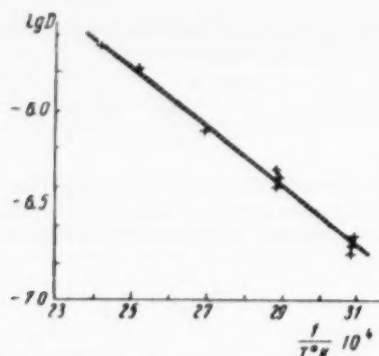


FIG. 4.—The abscissa represents $1/T \times 10^4$, where T is in $^{\circ}\text{K}$; the ordinate $\lg D$.

$u = 7000 (\pm 1000)$ cal./mole. The value for the diffusion coefficient of sulfur in natural rubber at various temperatures is given quantitatively by the equation: $D = 0.0107 e^{-7000/RT}$ cm.²/sec.

The diffusion coefficient of sulfur in rubber was practically independent of the sulfur concentration, up to a sulfur content of 10 per cent.

By a similar method we studied the diffusion of sulfur in a soft vulcanizate (cured natural-rubber). The diffusion coefficient in this material was slightly lower than that of raw rubber, and could be expressed by the equation: $D = 0.0060 e^{-7000/RT}$ cm.²/sec. This same method was applied also to synthetic (sodium-butadiene rubber, i.e., polybutadiene) rubber. In this too, the sulfur diffusion proceeded at approximately the same rate, and at various temperatures it conformed to the relation: $D = 2.91 e^{-15,900/RT}$ cm.²/sec.

Finally, we prepared from labeled sulfur (S^{32}) the accelerator tetramethylthiuram disulfide, whose diffusion was likewise measured at two temperatures; it was found that $D = 0.74 \times 10^{-6}$ cm.²/sec. at 115°C , and $D = 1.3 \times 10^{-6}$ cm.²/sec. at 125°C .

Consequently, the thiuram molecules diffuse at approximately the same rates as do the sulfur molecules. As will be seen later, this agreement is quite strict.

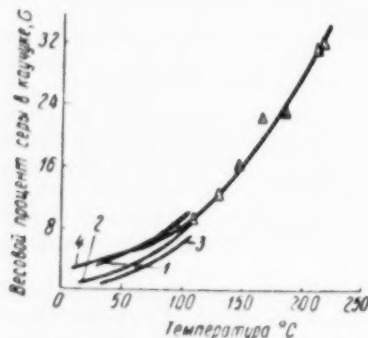


FIG. 5.—1—data from the literature²; 2—from³; 3—from⁴; 4—from⁵. Points marked with triangles—our data. The abscissa represents temperature in $^{\circ}\text{C}$; the ordinate the percentage by weight of sulfur in the rubber, σ .

By utilizing labeled sulfur it is possible to determine, by a fairly simple method, the equilibrium solubility of sulfur in rubber. The literature data on the solubility of sulfur are contradictory and extend only up to a temperature of 120° C. We employed the following method. A sample of rubber, on the bottom surface of which had been placed a large excess of labeled sulfur, was placed in our usual apparatus and heated to the necessary temperature.

An interval of heating time was chosen such that the concentration of sulfur became uniform throughout the sample, and at this time a final measurement of radioactivity was made. Then the temperature of the constant-temperature bath was raised, and, after the necessary elapsed time, the next measurement was made, and so forth. In this way the progress of solubility versus temperature can be derived in a short time without removing the sample from the constant-temperature apparatus.

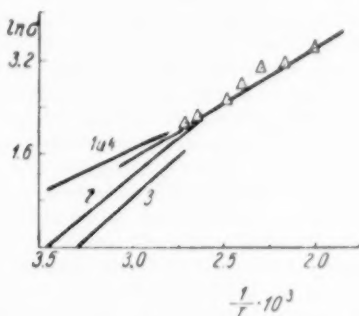


Fig. 6.—The designations are the same as in Figure 5. The abscissa represents $1/T \times 10^3$; the ordinate in σ .

Such measurements gave, of course, only the relative solubility. In order to obtain absolute values, it was necessary to carry out a calibration method. For this purpose a set of rubber samples containing 1 to 10 per cent by weight of radioactive sulfur were prepared. In these cases, in contrast with those before, the sulfur was introduced in such amounts as to be completely soluble in the hydrocarbon.

The radioactivity of the prepared samples was measured in the same apparatus, with a strict adherence to the same geometric conditions, but the sulfur concentration was determined gravimetrically. This made it possible to set up a calibration for the conversion from the measured radioactivity of a sample to the concentration of sulfur by weight. The calibration curve, as one might expect, proved to be linear.

With such a procedure the solubility curve shown in Figure 5 was obtained. It coincides approximately with the data from earlier work, but with a considerable broadening of the range of temperatures investigated. Figure 6 gives curves of $\ln \sigma = f(1/T)$, corresponding to the curves in Figure 5.

We are convinced that the solubility of sulfur in rubber at various temperatures can be expressed by the equation:

$$\sigma = \sigma_0 e^{-\frac{u}{RT}} = 1.17 \cdot 10^3 e^{-\frac{3700}{RT} \sigma_{r/c}^0}$$

THE COMBINATION OF SULFUR WITH RUBBER

During the period of time that was necessary in the experiments for obtaining curves of diffusion (0.5–1.5 hours), practically no vulcanization took place in a pure rubber. We became convinced of this by measuring the radioactivity of the sample on both sides after the diffusion process had come to an end. The distribution of sulfur, after the conclusion of the process, was found to be completely uniform; accordingly, the concentration of sulfur at both surfaces was found to be the same.

A different result was obtained, however, when an accelerator was introduced by milling into the sample—tetramethylthiuram disulfide (thiuram) or mercaptobenzothiazole (Captax), in the quantities usually used for vulcanization (0.3–0.5 per cent). Then the sulfur, while diffusing from the bottom to the top surface of the sample, irreversibly combined at the same time with the polymer and gradually left the system, thus ceasing to take part in the diffusion. For this reason, the final distribution of sulfur in the sample proved to be markedly asymmetrical. The final radioactivity of the sample on its bottom side, where the radioactive sulfur was located at the outset, was found to be several times greater than at the top surface, which the sulfur had reached as a result of diffusion. An investigation of the asymmetry of the final distribution of sulfur in the sample gave us a method of quantitatively studying the kinetics of the combination of sulfur with rubber. The great advantage of this method lies in its extreme simplicity. There is no necessity of removing the unreacted sulfur from the sample, and generally there is no chemical manipulation involved. The simple determination of radioactivity near the surface of the sample makes it possible to calculate at the same time the rate constant for the reaction. This method can, no doubt, find a wide application in the study of rates of reaction in the solid phase, and particularly the rates of various reactions in polymers.

If the amounts of sulfur chosen for an experiment are small, then the rate of combination may be considered proportional to the concentration of free sulfur at each point in the sample, i.e., it may be assumed that the combination proceeds as a first-order reaction, as regards sulfur.

An equation expressing the concentration of free sulfur as a function of time will have the following form:

$$\frac{\partial Q}{\partial t} = D \frac{\partial^2 Q}{\partial x^2} - \beta Q$$

the boundary conditions remaining the same as they were previously:

$$\left. \frac{\partial Q}{\partial x} \right|_{x=0} = \left. \frac{\partial Q}{\partial x} \right|_{x=d} = 0 \quad \text{and} \quad Q|_{t=0} = Q_0(x)$$

where Q is the concentration of free sulfur; β is the rate constant for the reaction of sulfur combination.

Solving the equation under conditions of "large" periods of time, we find an expression for the radioactivities as measured at the surfaces:

$$I(t, 0) = I_1 + Ke^{-\left[\left(\frac{\pi}{d}\right)^2 D + \beta\right]t}$$

$$I(t, d) = I_2 - Ke^{-\left[\left(\frac{\pi}{d}\right)^2 D + \beta\right]t}$$

where $I(t, 0)$ and $I(t, d)$ are the radioactivities as measured at the surfaces $x = 0$ and $x = d$; $I_1 = I_1(\beta, d)$ and $I_2 = I_2(\beta, d)$ —their limiting values.

Knowing the ratio between I_1 and I_2 (measured over a long period of time), and the angle of slope of the straight line of $\ln [1 - (I/I_2)]$ versus t , it is easy to calculate the diffusion coefficient and the rate constant for the reaction of sulfur combination, β . The details of the calculation technique we have outlined in the mathematical supplement (see section on mathematical treatment).

We will now describe the procedure used for the experiment in which the kinetics of sulfur combination was investigated. The apparatus employed in this case was no different from that in which the diffusion of sulfur in rubber was measured. An accelerator (thiuram in the amount of 0.4 per cent or Captax, 0.5 per cent) was introduced by milling into natural rubber samples of different thicknesses (0.4 to 1.5 mm.). Radioactive sulfur, in an amount not exceeding 0.05 per cent on the weight of the sample, was placed on the bottom surface of the sample. The measurement of the progress of the radioactive sulfur to the top surface was carried on continuously with the aid of the counter. Besides this, at the conclusion of the experiment a careful measurement was made of the asymmetry of the distribution; i.e., the difference between the radioactivities of the two surfaces. Plotting the quantity $\ln [1 - (I/I_2)] = f(t)$ as before, we obtained straight lines. In this case the lines did not pass through $\ln 2$. By determining the tangent of the angle of slope of these lines and the asymmetry of the distribution, we found the quantities D and β .

There are several ways in which the flawless accuracy of both the experimental data and the method of handling them can be confirmed. In the first place, the values found for samples of different thicknesses agree well with one another. In the second place, the values for the diffusion coefficient of free sulfur, D , proved to be the same as those obtained from the studies of pure diffusion without chemical reaction. In Figure 4 the points obtained in these experiments are shown, along with other points; these fall on the selfsame curve, that of the effect of temperature on D . A third control method is based on the fact that the initial ordinate values of the logarithmic straight lines of $\ln [1 - (I/I_2)] = f(t)$ are calculated from the quantities which we found for D and β . The calculated value was found to be in satisfactory agreement with that derived from experiment. In Figure 7 we present, in terms of $\log \beta$ versus $1/T$, the relation between the rate constant for sulfur combination with rubber and the absolute temperature, for experiments with thiuram. The Arrhenius law $\beta = \beta_0 e^{-U/RT} = 2.7 \times 10^8 e^{-23,000/RT} \text{ sec.}^{-1}$ was satisfactory. The energy of activation $U = 23,000 \pm 1500 \text{ cal./mole}$. This quantity agrees nicely with the data known from the literature, which were derived by way of the usual chemical extraction methods for the study of the kinetics of sulfur combination. In experiment with Captax, likewise, satisfactory kinetic data were obtained, which may be described by the equation:

$$\beta = \beta_0 e^{-\frac{U}{RT}} = 1.4 \cdot 10^8 e^{-\frac{22,000}{RT}} \text{ sec.}^{-1}.$$

Introducing the rate constant β , we were dealing with the process of sulfur combination in a purely descriptive manner. We did not take into account here the role of the accelerator (thiuram). As we shall see later, the decomposition of the thiuram into radicals and the reaction of these with molecular sulfur is itself the basic reaction of the combination process.

Hence we may consider the reaction of sulfur combination to be a first-order reaction, with respect to both the sulfur and the thiuram. That is, we may

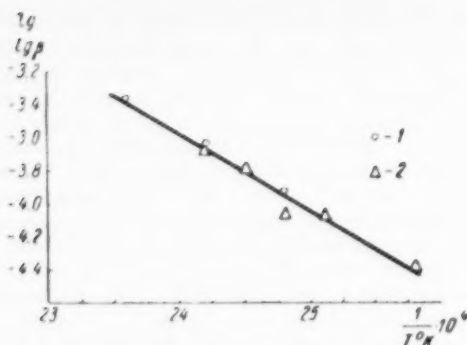


FIG. 7.—The abscissa represents $1/T \times 10^4$ ($T = ^\circ \text{K}$); the ordinate represents $\log \alpha C$ (for the points numbered 1) and $\log \beta$ (for 2).

assume that the rate is equal to $\alpha'QC$, where C is the thiuram concentration; α' is the true rate constant; and Q is the free sulfur concentration.

The constant β , which we found earlier, may be expressed in the following terms:

$$\beta = \alpha' C.$$

In order to distinguish the mechanism of the reactions between the sulfur and the accelerator, we made a separate study of the isotope exchange reaction between thiuram and labeled elemental sulfur; i.e., the replacement of sulfur in the thiuram molecule with labeled sulfur. We carried out the reaction in an inert liquid solvent—paraffin oil. The temperature range was the same as that in which the combination constant β was measured.

As the next paragraph shows in detail, the isotope exchange reaction between thiuram and elemental sulfur proves to be a first-order reaction with respect to the thiuram and the sulfur; i.e., the rate of the reaction may be described by the expression αQC . The quantity α was measured at several temperatures.

Here the following fundamental fact was revealed: the rate constants of these two quite different processes were shown to be exactly the same. The congruence between not only the energies of activation for both processes, but also between their absolute constants, i.e., their activation constants at absolute zero in the Arrhenius equation, was especially remarkable.

In Table 2 are presented the values of β , together with the values of α derived from isotope exchange experiments, as well as the products αC , where C is the thiuram concentration (0.4 per cent) used in our experiments on the kinetics of the combination.

TABLE 2

T ($^\circ \text{C}$)	$\alpha \times 10^4$ (1/sec. mole)	$\alpha C \times 10^4$ (1/sec.)	$\beta \times 10^4$ (1/sec.)
150	4.6	3.7	—
140	2.3	1.8	2.1
135	—	—	1.6
130	1.1	0.89	0.85
125	—	—	0.86
115	—	—	0.42

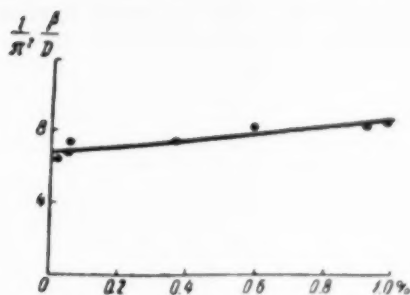


Fig. 8.—The abscissa represents the percentage sulfur by weight of the rubber; the ordinate $1/\pi^2 \cdot \beta/D$.

Table 2, and in particular Figure 7, demonstrate the complete agreement between the rate constants of the two reactions.

In further experiments we investigated the rate of sulfur combination with rubber for high sulfur concentrations, up to 5 per cent by weight. It was found that the behavior under these conditions is quite complex. Although with low sulfur concentrations the quantity β was independent of sulfur concentration, nevertheless when we went to higher concentrations we obtained higher and higher values for β (Figure 8).

This attests that the reaction of sulfur combination, in fact, proceeds not according to the first order, but to a greater degree in dependence on the concentration. Only at low sulfur concentrations is the process fairly close to linearity, and it may be then characterized by the rate constant β .

With sulfur concentrations of the order of 1 per cent, the very idea of calculating β from the kinetic curves becomes absurd, since they cease to conform to the theoretical relation $\ln [1 - (I/I_2)] = f(t)$, which we had used earlier. These deviations of the kinetic characteristics of the process from those considered earlier, which satisfied a linear kinetic equation, may be considered as the superimposition of some kind of secondary reaction, in which extra sulfur

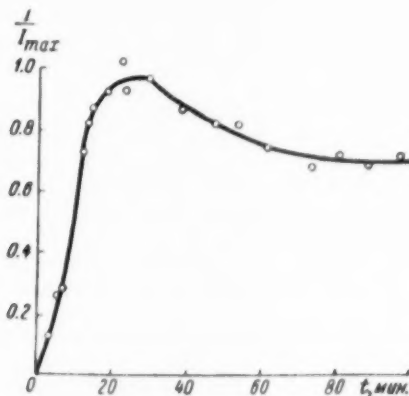


Fig. 9.—The abscissa represents time in minutes; the ordinate I/I_{\max} .

combines at the very places where it had combined before with the hydrocarbon, on the primary sulfur combination reaction. Such a viewpoint (whose concrete physical significance we shall deal with later) fully explains the non-linearity of the overall process of sulfur combination with rubber. However this demands special evidence. Such evidence can be successfully obtained by studying the sulfur diffusion process in a sample with an accelerator, at a sufficiently high sulfur concentration (3 per cent).

Here the following new phenomenon was discovered (Figure 9). The radioactivity at the top surface of the sample rose at first, as we had observed earlier, but then reached a maximum and started to fall. The final radioactivity at the top surface was about 25 per cent lower than the maximum. This signifies that, at some moment of time, the free sulfur concentration at the bottom surface of the sample, from whence the diffusion process started, has fallen to a lower level than the concentration at the top surface, with the result that diffusion of sulfur in reverse, from the top down, occurs. Such a process can

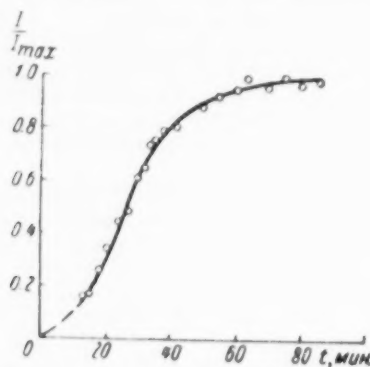


Fig. 10.—The abscissa represents time in minutes; the ordinate I/I_{max} .

be understood in no other way than as an additional secondary combination of sulfur at those places in the sample where the primary combination has taken place, with the result that the free sulfur concentration declines especially sharply from the maximum point. No sort of linear combination reaction can account for such a course of events.

We took many careful measures to avoid any possible source of error, particularly the escape of sulfur at the top surface of the sample.

The best control method for the reliability of our experiments proved to be that based on the fact that the synthetic rubber, polybutadiene (SKB), when investigated under identical conditions, gave a normal type of radioactivity curve, without any maximum (Figure 10). In relation to this, it was revealed that the combination of sulfur with this SKB rubber conformed to a linear kinetic equation for the whole of the sulfur concentration range under investigation (i.e., 3-5 per cent).

These facts attest that, in addition to the primary reaction of the combination of sulfur with natural rubber, there exists also a supplementary secondary combination reaction. In SKB rubber this secondary combination does not appear.

THE ISOTOPE EXCHANGE REACTION BETWEEN THE ACCELERATORS AND THE SULFUR

The clarification of the mechanism of the interaction between sulfur and accelerators involved a study of the isotope exchange reaction between the accelerator (thiuram) and elemental sulfur, labeled with the radioactive isotope S^{35} . In the literature are found just two works on the exchange between thiuram and radioactive sulfur⁷. Neither of these was satisfactory for our situation, since neither made it clear just how close to an equilibrium of exchange the authors were able to come. Since the question of the equilibrium state of the results obtained was not checked with any kind of control, it was impossible to draw any sort of quantitative conclusions from the data obtained in this work.

In the first paper it was shown that melting thiuram with sulfur caused an exchange of two of the thiuram's four sulfur atoms with the labeled sulfur. In the second, the authors came to a contrary conclusion as to the exchangeability of all four sulfur atoms in thiuram. It is easily shown, by analysis of the authors' data, that the assumption that the reaction is 25 per cent incomplete is sufficient to disprove the latter conclusion. With such an incompleteness of reaction assumed, the figures obtained by these authors agree well with the assumption that only two atoms of sulfur exchange with each thiuram molecule. In order for such experiments to attain the status of evidence, it is necessary that they be tied in with a quantitative study of the kinetics of isotope exchange, from which might be deduced also the conditions of the final equilibrium distribution of the tagged sulfur.

We instituted a systematic investigation of the kinetics of the isotope exchange reaction between elemental sulfur and thiuram.

THE EXPERIMENTAL METHOD

The exchange reactions between thiuram and sulfur were carried out in an inert solvent (paraffin oil) at temperatures of 130–150° C, which are characteristic temperatures for the vulcanization process. We employed the apparatus depicted in Figure 11.

In one arm of the apparatus was placed a solution of thiuram in oil; in the second, a solution of radioactive sulfur in the same oil. The vessel was placed in a constant-temperature bath for 0.5 hour, after which the contents of both sections were mixed together, without removing the apparatus from the constant-temperature bath. At certain intervals of time the experiment was interrupted, and the contents of the apparatus were subjected to fractionation. The quantity of air remaining in the apparatus after it was filled was negligible. The apparatus was tightly sealed with ground-glass stoppers. The experiment showed that there were no gases present at all, and in particular no hydrogen sulfide, after 30–60 minutes' heating.

The principal experimental difficulty was the separation of the accelerator from the elemental sulfur and from the oil. This was achieved in the following manner. The oil was agitated with hot methanol at its boiling point (72° C). Then the methanol was separated hot from the oil layer. The methanol removed an appreciable portion of the thiuram from the oil, but removed practically no elemental sulfur. (We were convinced of this by special control experiments with only sulfur and no thiuram.) After the methanol solution was cooled, the thiuram separated in the form of a crystalline precipitate. Since methanol dissolves a small amount of oil, for the greatest purity of the experi-

ment we had to separate the thiuram crystals from the methanol and redissolve them in fresh portions of the alcohol. Here, to avoid having to weigh precipitates, we first determined the solubility of thiuram in methanol at 20° C, and then simply saturated the methanol with the thiuram under investigation in a constant-temperature apparatus at 20°. Then we placed a certain volume (0.1 ml.) of the saturated solution on a small plate for the radioactivity measurement.

By using the value for the solubility of thiuram in methanol (2.4 mg./ml.), we were always able to tell exactly how many milligrams of thiuram were deposited on the plate and, consequently, how many milligrams of sulfur were there. The radioactivity of the precipitates was measured with different quantities of thiuram deposits so that, having constructed a curve of this, we could be sure that we were operating in a linear region, where the radioactivity of a precipitate was proportional to its weight. The radioactivity of the original elemental sulfur was determined with the very same counter and plates, and with a strict repetition of all the geometric conditions.



Fig. 11.—(No caption given; this is the vessel for thiuram exchange experiments.)

The radioactive sulfur must be diluted 30-fold with inert sulfur, after which it is placed on the plate in the form of a finely dispersed suspension in methanol.

The experiments on the exchange between thiuram and rubber were set up with various concentrations of sulfur and thiuram, so as to find out the order of the reactions.

In this way we obtained detailed information on the kinetics of the isotope exchange reaction at three temperatures: 150°, 140°, and 130° C. The crystalline precipitate, which separated out from the methanol on cooling, was subjected to elemental analysis, which confirmed the fact that it was indeed tetramethylthiuram disulfide.

TREATMENT OF THE EXPERIMENTAL DATA

It is not difficult to write the kinetic equations for the isotope exchange between thiuram and sulfur. In doing this, we assume that the exchange reaction is bimolecular.

Let n_1 represent the number of sulfur atoms in 1 ml. that belong to the thiuram and are capable of exchanging with free sulfur; a_1 the number of atoms of radioactive sulfur in the thiuram, in 1 ml.; $n_1 - a_1$, the number of atoms of

nonradioactive sulfur in the thiuram; n_2 the number of atoms of free sulfur in 1 ml. of the solution; a_2 the number of atoms of radioactive free sulfur in 1 ml.; and $n_2 - a_2$, the corresponding number of atoms of nonradioactive sulfur. Then the differential equation for the exchange is written in the following form:

$$\frac{da_1}{dt} = \alpha[(n_1 - a_1)a_2 - (n_2 - a_2)a_1].$$

In the initial moment, all the atoms of radioactive sulfur exist in the form of free sulfur. Letting a_0 represent the number of these in 1 ml. of solution, we may substitute:

$$a_2 = a_0 - a_1.$$

Our differential equation is then written as:

$$\frac{da_1}{dt} = \alpha n_1 a_0 - \alpha a_1(n_1 + n_2).$$

Integrating it with the initial condition $a_1|_{t=0} = 0$, we get:

$$a_1 = \frac{n_1}{n_1 + n_2} a_0 (1 - e^{-\alpha(n_1 + n_2)t}).$$

The solution can be written conveniently in other symbols. Taking I_0 as the radioactivity of 1 mg. of the sulfur used in the experiment; I_1 as the radioactivity of 1 mg. of thiuram after its removal from the reaction mixture; p_1 as the weight of the thiuram used in the experiment; p_2 as the weight of the sulfur used in the experiment; V as the volume of the oil (the solvent); N as the Avogadro number; x as the number of sulfur atoms in a thiuram molecule that are capable of isotope exchange; and considering that the ratio of the molecular weight of thiuram to the atomic weight of sulfur $240/32 = 7.5$ —we may write the final expression:

$$I_1 = I_\infty \left[1 - e^{-\frac{\alpha N \left(p_1 + \frac{7.5}{x} p_2 \right)}{1.2 \cdot 10^4 V} t} \right] = \frac{I_0}{\frac{7.5}{x} + \frac{p_1}{p_2}} \left[1 - e^{-\frac{\alpha N \left(p_1 + \frac{7.5}{x} p_2 \right)}{1.2 \cdot 10^4 V} t} \right].$$

Plotting $\log [1 - (I_1/I_\infty)]$ as a function of time, we should obtain, for a constant temperature, a straight line which passes through the origin. Here we can, at the same time: (1) verify the bimolecular character of the isotope exchange reaction, choosing various weight ratios of thiuram to sulfur, and (2) show, by means of the experimental data, that the quantity $x = 2$.

This latter conclusion was demonstrated with great precision, since the comparatively small error in I_∞ caused an appreciable inflection in the graph of $\log [1 - (I_1/I_\infty)] = f(t)$.

RESULTS OF THE EXCHANGE EXPERIMENTS

In Figure 12 are drawn the straight lines of $\log [1 - (I_1/I_\infty)] = f(t)$ at three temperatures: 130°, 140°, and 150° C. In Table 2 and in Figure 7 are presented the values of the rate constant α as calculated from these.

Each point on the straight lines of Figure 12 represents a separate experiment. Along with these, in order to have evidence of the bimolecularity of the

exchange reaction (i.e., the fact that it is a first-order reaction with respect to both the sulfur and the thiuram at the same time), we set up experiments at only one temperature. In these the quantity V —the volume of the solvent—varied widely (0.7–3.4 ml.); as did p_1 , the weight of the thiuram (4.46–27.5 mg.); and p_2 , the weight of the sulfur (0.7–3.4 mg.).

As can be seen in Figure 12, the kinetic data coincide nicely with the equation for a bimolecular reaction, thus proving without a doubt the accuracy of our expression for the rate of reaction.

Hence no doubt whatever remains that the thiuram is capable of exchanging only two sulfur atoms ($x = 2$).

The influence of temperature on the values of the rate constant for isotope exchange, α , may be expressed (Figure 7) by the Arrhenius equation:

$$\alpha = \alpha_0 e^{-\frac{U}{RT}} = 3.2 \cdot 10^9 e^{-\frac{23,000}{RT}} \frac{1}{\text{sec.-mole}}$$

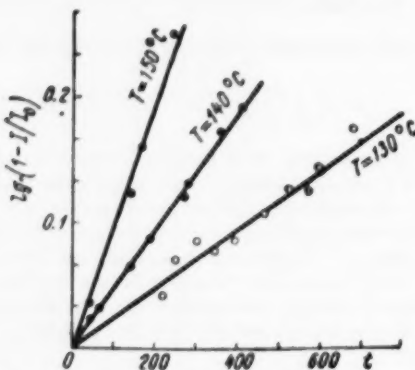


FIG. 12.—The abscissa represents time; the ordinate $\log(1 - I/I_0)$.

ANALYSIS OF THE EXPERIMENTAL RESULTS

From the experimental data presented above, one can draw some detailed conclusions regarding the mechanism of vulcanization. Let us consider the process in stages. Without a doubt, the first stage of the vulcanization process is the dissolving and diffusing of the sulfur in the rubber. It may be asked, can the diffusion or the solution of the sulfur be the limiting reaction in vulcanization; i.e., can this by itself govern the overall reaction rate? Now we may flatly reject such a possibility on the basis of direct experiment. In the industrial vulcanization process, the finely powdered sulfur is dispersed in the rubber. If C represents the sulfur concentration by weight during vulcanization; δ , the specific gravity of sulfur; and d , the size of the sulfur particles, then it is not hard to write an expression for the mean distance between two particles of dispersed sulfur: $d' = d\sqrt[3]{\delta/C}$. In order for the sulfur to be thoroughly mixed in the rubber, it is necessary that the diffusion should pass through a mean distance of $d'/2$. This requires a length of time which is known to be equal to $\tau = (d'/2)^2/2D$, where D is the diffusion coefficient of the sulfur in the rubber. For a temperature of 130°C, we may substitute the values: $C = 3\%$, $\delta = 2.2$ g./cc., $D = 2 \times 10^{-6}$ cc./sec., $d = 0.1$ mm. Whence $\tau = 5$ seconds. The process of sulfur going into solution, i.e., the transition of sulfur molecules from

sulfur to hydrocarbon, goes considerably faster still than does the diffusion of sulfur in rubber. We may confirm this by the fact that the process of the diffusion of sulfur from the surface, where the sulfur is in excess, must conform to a boundary condition which governs the constancy of the concentration at this boundary. This also denotes that, in the immediate vicinity of the sulfur crystals, a saturation concentration of sulfur in the rubber is achieved almost instantaneously and is maintained at all times.

Consequently, the equilibrium distribution of sulfur in the rubber, under the actual conditions of the industrial process, is established within a few seconds after the start of the process, while the chemical reaction lasts for tens of minutes. Thus the actual vulcanization should be considered as a homogeneous process. The heterogeneous stage passes so quickly that it can have no effect on the total rate of the process.

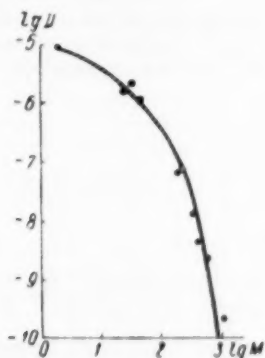
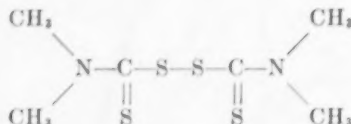


Fig. 13.—The abscissa represents $\lg M$ (M = molecular weight); the ordinate $\lg D$.

From a consideration of the diffusion constant, one can draw some essential conclusions as to the structure of the sulfur molecules diffusing in the rubber. It is known that sulfur as a liquid and as a vapor exists in the form of polyatomic molecules, principally as a ring, S_8 . In what form does the sulfur dissolve in the rubber? An answer can be given to this question, based on experiment. The diffusion coefficient of a variety of substances in liquids and in polymers is governed in a definite manner by the molar volume of the diffusing substance or, in a rough approximation, by its molecular weight.

Figure 13 presents a curve of relation between the diffusion coefficients of various substances in rubber and their molecular weights. This sketch shows that there is a definite correlation between the two quantities, for diffusing substances with molecular weights⁸ ranging from 2 to 2000. Since the curve was constructed from literature data obtained at 25° C, we extrapolated the diffusion coefficients found by experiment for thiuram and for sulfur, and found the positions of the corresponding points for these on the curve. For thiuram, $D_{25^\circ} = 0.66 \times 10^{-7}$ cm.²/sec., from which we derived the molecular weight $M = 260$, instead of the true value of 240. We can see that, in this case too, the agreement is sufficiently good. Now we calculated the molecular weight for the diffusing sulfur. For sulfur in rubber, $D_{25^\circ} = 0.78 \times 10^{-7}$ cm.²/sec., whence $M = 250$. We can see that our experiment confirms the existence of molecules of S_8 as the main structural units which dissolve and diffuse in rubber.

The next fundamental fact found in the experiments described above is the fact that the rate constant for the combining of sulfur with rubber is equal to the rate constant for the isotope exchange of sulfur with the accelerator (thiuram). As we have already noted, the experiments not only show a congruence between the activation energies for both processes, but also an agreement between the absolute values of the constants (i.e., the exponential values). This agreement leaves no doubt that the basic process which determines the rate of vulcanization is the reaction between the elemental sulfur (present in the form of complex S_8 molecules) and the accelerator. Besides this, we were able to confirm the fact that the basis for both reactions—vulcanization and isotope exchange—is to be found in this same single limiting process. It was logical to assume that the first stage of both chemical reactions was the process of decomposition of the thiuram accelerator into radicals. This fission should proceed in a monomolecular way. We were able to tell, furthermore, just how the thiuram disulfide does break up into radicals. Finally, our experiments showed that two of the four sulfur atoms in the thiuram can exchange with elemental sulfur. It should follow that the two atoms which undergo exchange are those of the disulfide bridge:

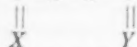


From this it follows that the splitting of the thiuram into radicals can be assumed to proceed according to the equation:



No other reaction for the splitting of thiuram into radicals can be considered probable. For if the splitting occurred in the center of the disulfide bridge, i.e., if $(\text{CH}_3)_2\text{N}(\text{CS})-\text{S}\cdot$ radicals were formed, then all four of the sulfur atoms in the molecule would inevitably enter into the isotope exchange, since in such radicals both sulfur atoms would be situated in the same position on the carbon atom.

The equation which we have written for the decomposition of thiuram into radicals agrees with the known facts of organic chemistry. The cleavage of thiuram and of similar compounds of the type $\text{R}_1-\text{C}-\text{S}-\text{S}-\text{C}-\text{R}_2$, contain-

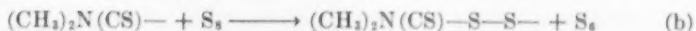


ing the substituents X and Y, by the action of water and of alkalis, shows that the reaction proceeds with the splitting off of sulfur, and that it undoubtedly goes through a radical stage as described in Equation (a)⁹.

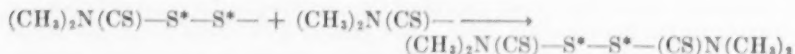
The result of the decomposition of thiuram is the appearance of "active sulfur" in the form of diatomic fragments, which are very far removed from the thermodynamically stable form (the S_8 ring), and therefore constitute active radicals.

When disulfide compounds of a different type, such as ethyl disulfide¹⁰, decompose, the cleavage is at the center, without any sulfur being given off. Accordingly, such compounds are found not to be vulcanization accelerators. Now we may describe the concluding stages of the exchange and combining

processes. The second stage may logically be supposed to be the following reaction:



The $(\text{CH}_3)_2\text{N}(\text{CS})\text{—}$ radical attacks the S^*_8 rings and splits off sulfur atoms from them. There is a high probability that this reaction will take place, since the reaction between the free radical and the sulfur molecule requires only a very low activation energy. And finally, the third reaction—the recombination of the radicals—should convert them back into a thiuram with exchanged sulfur in the bridge:



Such a sequence of reactions offers a good explanation of the observed facts. First, it is plain that the rate of the isotope exchange reaction and that of the reaction of sulfur combination with rubber are of the first order with respect to the concentrations of sulfur and thiuram. Further, both reactions have the very same rate constant, since they both proceed in an identical manner. The S_2 group, liberated as a result of the reaction detailed above, has the properties of a free radical, and it unites with the rubber in some way. The details of this reaction and the chemical structure of the resulting products are unknown at the present time.

The experiments described above demonstrate that the reaction of rubber with sulfur has not been exhaustively covered by our analysis of it as a linear combination reaction (proceeding according to a first-order equation with respect to sulfur and thiuram). The linear combination of sulfur is prevalent only at very low concentrations of sulfur (less than 0.1 per cent). At the usual sulfur concentrations for the vulcanization process, 2–5 per cent, the secondary process of sulfur combination, at points where the sulfur is already bonded to the rubber, plays a greater role.

The curve of Figure 9 represents direct experimental evidence of such a secondary sulfur combination. We are now able to evolve a preliminary hypothesis as to the mechanism of this secondary combination and the part that it plays in the vulcanization of natural rubber.

Earlier we considered the primary combination of sulfur with rubber in the form of the biradicals —S—S— . After such a combination, one might assume that the corresponding point on the chain itself would take on the properties of a very active free radical, and be capable of an activating influence on the saturated sulfur molecule, S_8 . When this happens, the S_8 ring should break open to form a biradical, which is able to unite the small chain of sulfur atoms with two fragments of hydrocarbon chains which have been activated by the primary sulfur combination.

Consequently, one may suppose that the vulcanization bridges in the rubber are formed by the recombination of polysulfide radicals, and have a length of 10 to 20 atoms of sulfur.

The possibility of the existence of polysulfide bridges, together with simple ones, had been recognized earlier by various authors, notably Dogadkin¹⁴.

This explains the chemical analysis data which indicated that only a small part of all the combined sulfur was actually bonded to carbon.

Seen from the viewpoint of the concept of polysulfide vulcanization bridges, the facts known from the literature begin to seem quite reasonable.

(1) The liquefaction of vulcanizates by the action of accelerators⁸ finds its cause in the reaction between the accelerator and the sulfur of the bridges. Such a reaction is evidently quite possible, and leads to a rupture of the bridges; i.e., to the reversion of vulcanization.

(2) The remarkable kinetic regularities found by Spence and Young² evidently result from this same reaction between the accelerator and the sulfur bonded in polysulfide bridges. Now, the rate of the sulfur combination with rubber, as we have seen, is governed by the basic reaction between sulfur and accelerator. But only a small part of all the combined sulfur is actually bonded directly to the hydrocarbon itself. The greater part of the combined sulfur exists in the form of secondarily (indirectly) combined polysulfide bridges. This polysulfide sulfur is no less capable of reacting with thiuram radicals than is elemental sulfur. Consequently, the rate of the sulfur combination reaction will not depend on time, since this combined sulfur is perfectly capable of entering into a reaction with a catalyst. Such is the logical explanation of the kinetic curves of the overall reaction of sulfur combination with rubber.

The formation of polysulfide bridges between double bonds was studied via organic chemistry, on simple type reactions. Thus, for example, a detailed study was made of the combining reaction between sulfur and isopentene, $\text{CH}_3-\text{CH}=\text{C}-\text{CH}_3$, at a temperature¹² of 130° C.



This should give rise to structures similar to those which take shape when polyisoprene is vulcanized. It was possible in this experiment to fractionate the reaction products by vacuum distillation and to study their structure. It was found that at first complex molecules are formed, made up of two molecules of isopentene tied together by a small polysulfide chain. The experiment showed also that the number of sulfur atoms required for one pair of pentene molecules is greater than six.

The activation energy for the vulcanization of natural rubber without accelerators is 30,000 cal./mole, and this agrees fully with the energy for the rupture of the S_8 ring. This is interpreted by many chemists¹³ as being the union of the rubber with a biradical created by the rupture of the ring. (The energy for the rupture of the ring, or that for the rupture of a polysulfide bond, equals 27,500 (± 5000) cal./mole for each¹⁴.) Unfortunately, not knowing the chemical structure of the resulting compounds, we are unable to go into a quantitative analysis of the known data on heats of vulcanization. Let us only point out that the heat given off during the sulfur combination amounted to 20 cal./g. of rubber, where the combined sulfur was 3 per cent.

This gives, let us say, 20,000 cal./g.-atom of sulfur, which is not comparable to the energy of the C—S bond (54,000 cal./mole) nor to the energy of the disulfide bond S—S (64,000 cal./mole).

In the case of synthetic rubber, the experiment showed that the linear kinetics of the combination of sulfur with rubber holds true even at high sulfur concentrations. Hence we may suppose that the secondary sulfur combination, in the case of polybutadiene (SKB) is either nonexistent or else insignificant in amount.

MATHEMATICAL SUPPLEMENT

The process of diffusion of sulfur through rubber, in conjunction with the chemical combining of the sulfur, can be described by the differential equation:

$$\frac{\partial Q}{\partial t} = D \frac{\partial^2 Q}{\partial x^2} - \beta Q \quad (1)$$

with the boundary conditions:

$$\left. \frac{\partial Q}{\partial x} \right|_{x=0} = \left. \frac{\partial Q}{\partial x} \right|_{x=d} = 0 \quad (2)$$

and with the initial condition:

$$Q(x, 0) = Q_0 \delta(x) \quad (3)$$

where Q_0 is the amount of sulfur placed on 1 sq. cm. of the surface of the sample. From the determination of the δ -function:

$$\delta(x) = \begin{cases} 0 & \text{where } x \neq 0 \\ \infty & \text{where } x = 0 \end{cases} \quad \text{and} \quad \int_{-\infty}^{\infty} \delta(x) dx = 1.$$

By the Fourier method, a solution of the differential equation is easily found in the form of a series:

$$Q(x, t) = \frac{Q_0}{d} \left[\frac{e^{-\beta t}}{2} + \sum_{n=1}^{\infty} e^{-\left(\frac{n^2 \pi^2}{d^2} D + \beta\right)t} \cos \frac{n \pi x}{d} \right] \quad (4)$$

where $Q(x, t)$ is the concentration of free (i.e., diffusing) sulfur. We now find the concentration of combined sulfur at each point on the sample, which we designate by $Q'(x, t)$:

$$Q'(x, t) = \beta \int_0^t Q(x, t) dt = \frac{Q_0 \beta}{d} \left\{ \frac{1 - e^{-\beta t}}{2\beta} + \sum_{n=1}^{\infty} \frac{1}{\frac{n^2 \pi^2}{d^2} D + \beta} \left[1 - e^{-\left(\frac{n^2 \pi^2}{d^2} D + \beta\right)t} \right] \cos \frac{n \pi x}{d} \right\}. \quad (5)$$

The radioactivity of the sulfur near the surface, which we measured, was proportional to the summation of the concentrations of free and combined sulfur; i.e., to the quantity:

$$Q(x, t) + Q'(x, t) = \frac{Q_0}{d} \left\{ \frac{1}{2} + \sum_{n=1}^{\infty} \frac{\cos \frac{n \pi x}{d}}{1 + \frac{n^2 \pi^2 D}{d^2 \beta}} + \sum_{n=1}^{\infty} \frac{\frac{n^2 \pi^2 D}{d^2 \beta}}{1 + \frac{n^2 \pi^2 D}{d^2 \beta}} e^{-\left(\frac{n^2 \pi^2}{d^2} D + \beta\right)t} \cos \frac{n \pi x}{d} \right\}. \quad (6)$$

Now we find the asymmetry of distribution of the radioactivity at the end of the experiment; i.e., after a sufficient length of time has elapsed. We find the limit of the quantity $C = Q + Q'$ where $t \rightarrow \infty$.

$$C_{\infty} = (Q + Q')_{\infty} = \frac{Q_0}{d} \left[\frac{1}{2} + \sum_{n=1}^{\infty} \frac{\cos \frac{n\pi x}{d}}{1 + \frac{n^2 \pi^2 D}{d^2 \beta}} \right]. \quad (7)$$

The summation of the series was simple to obtain, and may be expressed by a hyperbolic function. For this we utilize the resolution into a Fourier series where $-d \leq x \leq d$.

$$Ch \sqrt{\frac{\beta}{D}} x = \frac{2Sh \sqrt{\frac{\beta}{D}} d}{\sqrt{\frac{\beta}{D}} d} \left[\frac{1}{2} + \sum_{n=1}^{\infty} \frac{(-1)^n \cos \frac{n\pi x}{d}}{1 + \frac{n^2 \pi^2 D}{d^2 \beta}} \right]. \quad (8)$$

Where $x = 0$, we get:

$$C_{\infty}(0) = Q_0 \frac{Ch \sqrt{\frac{\beta}{D}} d}{2Sh \sqrt{\frac{\beta}{D}} d} \sqrt{\frac{\beta}{D}}. \quad (9)$$

Where $x = d$, we get:

$$C_{\infty}(d) = Q_0 \frac{1}{2Sh \sqrt{\frac{\beta}{D}} d} \sqrt{\frac{\beta}{D}}. \quad (10)$$

The experimentally measured ratios between the radioactivities on either side of the sample (the asymmetry of distribution) equals:

$$\gamma = \frac{I_0}{I_d} = \frac{C_{\infty}(0)}{C_{\infty}(d)}.$$

From the above relation there follows this final simplified solution which we have utilized for the analysis of the experimental data:

$$\gamma = \frac{I_0}{I_d} = Ch \sqrt{\frac{\beta}{D}} d. \quad (11)$$

The value of the hyperbolic cosine may be got from tables; with the aid of a graph the quantity $\sqrt{(\beta/D)}d$ is found from the experimentally obtained values for the asymmetry, I_0/I_d . Since the diffusion coefficient D in experiments on sulfur combination should be identical to that which was measured in pure rubber without accelerators, we can, therefore, determine the reaction rate constant β , from only one measurement of the asymmetry of distribution of sulfur at the conclusion of the experiment.

We are able, however, to verify this for ourselves by another independent method. We measured experimentally the rise in the radioactivity I where $x = d$. Letting t be infinite in $e^{-\left[\left(\frac{n^2 \pi^2}{\beta}\right) D + \beta\right]t}$, i.e., making use of the rule

for great lengths of time, we get:

$$C(d, t) = C_{\infty} - \frac{Q_0}{d} \frac{\frac{\pi^2 D}{d^2 \beta}}{1 + \frac{\pi^2 D}{d^2 \beta}} e^{-\left(\frac{\pi^2}{\beta} D + \beta\right)t} \quad (12)$$

Letting the ordinate represent the quantity $\ln [1 - (I/I_{\infty})]$, as in the study of simple diffusion, we obtain for great lengths of time the straight line:

$$\ln \left(1 - \frac{I}{I_{\infty}}\right) = \ln \left[1 - \frac{C(d, t)}{C_{\infty}(d)}\right] = \ln 2Sh\sqrt{\frac{\beta}{D}}d \times \frac{1}{d\sqrt{\frac{\beta}{D}}} \frac{\frac{\pi^2 D}{d^2 \beta}}{1 + \frac{\pi^2 D}{d^2 \beta}} - \left(\frac{\pi^2}{d^2} D + \beta\right)t \quad (13)$$

From the slope of the straight line we obtain the quantity $(\pi^2/d^2)D + \beta$, and by another independent route we may determine the diffusion coefficient D in those experiments where a chemical combination of sulfur took place. From the data presented in this work, it is evident that the diffusion coefficients D , calculated from those same experiments in which the rate constant β was determined, agree with the values for D found in the previous set of experiments, in which only pure diffusion was being studied. Introducing the further designation, $\beta' = \sqrt{(\beta/D)}d$, we derived a comparatively simple expression for the initial ordinate value of the straight line:

$$\ln 2\pi^2 \frac{Sh\beta'}{\beta'(\pi^2 + \beta'^2)}$$

In contrast with the case of pure diffusion, the logarithmic straight line did not pass through $\ln 2$. Having determined the constants β and D , we are able to calculate how significantly the initial ordinate value of the straight line deviated from $\ln 2$.

In all of the experiments carried out, the measured and the calculated values for the initial ordinate agreed satisfactorily.

CONCLUSIONS

1. In the present work a method was developed for the measurement of the diffusion and the solubility of sulfur in rubber. Values of the diffusion coefficient and the solubility were obtained for a broad range of temperatures. It is shown that the free sulfur in rubber dissolves and diffuses in the form of S_8 molecules.

2. The kinetics of sulfur combination with rubber in the presence of an accelerator was investigated. It is shown that at low sulfur concentrations the kinetics is of the first order. The rate constants of sulfur combination were determined, as well as the activation energy ($U = 23,000$ cal./mole) of the process.

3. A study was made of the kinetics of the isotope exchange reaction between elemental sulfur and tetramethylthiuram disulfide in an inert solvent. The experiment showed that the rate constant of the isotope exchange and the

rate constant of the combination of sulfur with rubber are equal to one another at all the temperatures investigated (120°–150° C).

4. The conclusion is drawn that the first stage of vulcanization, which governs the overall rate, and likewise the first stage of the isotope exchange reaction, consist in the decomposition of thiuram into radicals, with the diatomic biradical S_2 being split off.

5. It is shown that, with an increase in the sulfur concentration, the kinetics of the sulfur combination with rubber ceases to conform to a linear equation. A secondary sulfur combination reaction, taking place at the point where the primary bonding of sulfur to rubber occurred, was discovered. A hypothesis is put forward as to the radical character of the primary sulfur combination, and regarding the union of polysulfide chains with the radicals in polymer chains, radicals which were formed by means of the primary action of sulfur upon the hydrocarbon.

ACKNOWLEDGMENT

V. P. Kushner, A. A. Polyak, I. A. Rozov, and E. M. Sominskii took part in this work.

REFERENCES

- ¹ Dogadkin, "Chemistry and Physics of Rubber", Goskhimizdat, 1947, p. 302; Bruni, *Rev. gén. caoutchouc* **8**, 19 (1931).
 - ² Spence and Young, *Kolloid-Z.* **11**, 28 (1912); **13**, 265 (1913).
 - ³ Sutherland, *J. Chem. Soc. (London)*, 1947, 1699.
 - ⁴ Tarbell and Harnish, *Chem. Rev.* **40**, 1 (1951).
 - ⁵ Williams, *Ind. Eng. Chem.* **39**, 901 (1947).
 - ⁶ Kemp and Malm, *Ind. Eng. Chem.* **32**, 1075 (1940).
 - ⁷ Mochel and Peterson, *J. Am. Chem. Soc.* **71**, 1426 (1949); Craig, Davidson, Juve, and Geib, *J. Polymer Sci.* **6**, 1 (1951).
 - ⁸ Grün, *Experientia* **3**, 490 (1947); *RUBBER CHEM. & TECHNOL.* **22**, 316 (1949).
 - ⁹ Tarbell and Harnish, *Chem. Rev.* **40**, 11 (1951).
 - ¹⁰ Guryanava, Syrkin, and Kuzina, *Doklady Akad. Nauk SSSR* **85**, 1021 (1952); **86**, 107 (1952).
 - ¹¹ "Investigations in the Physics and Chemistry of Rubber", edited by Evstratev and Dogadkin, Goskhimizdat, 1951.
 - ¹² Selker and Kemp, *Ind. Eng. Chem.* **39**, 895 (1947).
 - ¹³ Gordon, *J. Polymer Sci.* **7**, 485 (1951).
 - ¹⁴ Powell and Eyring, *J. Am. Chem. Soc.* **65**, 548 (1943).
- The following additional references are in the list of references but do not appear in the text:
- Loewen, *Kautschuk* **4**, 243 (1928).
- Williams and Kemp, *J. Franklin Inst.* **203**, 365 (1927).
- Morris, *Ind. Eng. Chem.* **24**, 584 (1932).
- Kemp and Malm, *Ind. Eng. Chem.* **32**, 1075 (1940).

PROTECTIVE ACTION OF ANTIOXIDANTS OF THE PHENOLIC TYPE ON THE AGING OF NATURAL RUBBER *

N. F. YARMOLENKA AND E. N. NOVIKAVA

The technological use of both natural and synthetic rubber is intimately tied in with the use of antioxidants or protective agents to inhibit the oxidation of the rubber by atmospheric oxygen.

Dogadkin and others¹ have shown that, in the absence of oxygen, rubber can deteriorate in the presence only of the most active radicals, and especially by the action of ultraviolet rays of wave length 4000 Å, which cause decomposition of the molecular chains of the rubber by absorption of quanta of light energy. This can be expressed as follows:



Ultraviolet radiation in the absence of oxygen, in the opinion of the authors, leads to rupture of the C—C bonds and the appearance of chain fragments, i.e., free radicals. The latter, by reacting with hydrogen, can form small molecules; at some concentrations of rubber, side-chain macromolecules can form during the reaction between the radicals.

Oxidation of any kind of rubber by molecular oxygen, as Kuzminskii and Lezhnev showed², takes place by addition of oxygen to the double bonds of the main chains of the polymer molecules. The degree of polymerization, the presence of double bonds in the side chains of certain types of rubber, and the presence of aromatic rings and other structural differences have practically no influence on the rate of oxidation of rubber.

Thus, the inhibiting action of antioxidants toward molecular oxygen involves the same mechanism for any type of natural or synthetic rubber.

In the selection of antioxidants, it is necessary to consider the general properties of the particular type of rubber (presence of double bonds in the main chains of the high polymer) as well as the general properties of all types of antioxidants. In our opinion³ such properties of antioxidants must include their oxidation capacity and the presence of polar groups.

Proceeding from the above considerations, we undertook a systematic study of the oxidation of rubber by atmospheric oxygen, with particular attention to the polar properties of the antioxidants which depend on the structure of the molecules containing the polar groups, to the nature and distribution of the molecular groups in the antioxidants, to the possibility of formation of different types of bonds between the molecules of antioxidant and rubber, to the type composition of antioxidants, etc.

Since not all the double bonds take part in the process of combination and the process is not as a rule continued to completion, this reaction can be ex-

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pressed in a general way by the following equation, without describing its particular individual stages⁴:



In a study of the heat oxidation of sodium-butadiene rubber by atmospheric oxygen⁵, Kuzminskii and others proved that in highly oxidized rubber a fraction of unsaturated bonds still remains. These authors showed that if a highly oxidized polymer is kept in a benzene solution of benzoyl peroxide, then is dried and is kept in solution a second time, benzoyl peroxide will promote further oxidation of the highly oxidized polymer.

There has been a tendency recently to regard the oxidation of rubber by atmospheric oxygen as a chain process, in which the double bonds, as a result of heat activation, react with molecular oxygen, forming rubber peroxide, RO_2 . In contact with the adjacent rubber molecules, these peroxide molecules activate the double bonds of the latter, with resulting formation of peroxides in the new molecules, and so on until the chain is deactivated and ruptured.

Although Margarytav⁶ tried to minimize the importance of oxidation in the aging process, his arguments are not convincing.

Experiments have shown that the destruction of rubber itself by oxidation results in the formation of volatile byproducts, for example, carbonic acid, water, hydrogen peroxide, and formaldehyde.

However, the action of the oxidizing agent is not observed in the earliest stage of oxidation.

Studies of the kinetics of oxidation of rubber films by atmospheric oxygen have demonstrated that, even in the presence of minimal quantities of absorbed oxygen, benzene solutions prepared from these films show a considerable decrease of viscosity in comparison with benzene-rubber solutions which are not in contact with oxygen.

If atmospheric oxidation is a fundamental cause of the aging of rubber and if it can be retarded by addition of antioxidants to the system, then the question of the mechanism of the inhibiting action of antioxidants arises.

Certain investigators seem to regard antioxidants as substances which themselves combine with atmospheric oxygen and thus serve as retarders, or else are capable of breaking the molecular chain, if it is assumed that oxidation of rubber by atmospheric oxygen is a chain process.

The rate of oxidation of the principal component of the system, the rubber, increases in proportion to the oxidation of the antioxidant added to the system.

The old theories of the inhibiting action of antioxidants of Garner, Porritt, and Bailey⁷ and others, who considered antioxidants to be either dispersers or ingredients which absorb the most active parts of the radiation, are not convincing.

There is a copious literature on studies of a large number of substances from the standpoint of their effect as antioxidants during the aging of Hevea rubber⁷.

It is noteworthy, that, in all types, the essential part of the molecule is a polar compound.

There is reason to believe³ that the mechanism of the action of antioxidants depends on the fact that they are oxidized themselves and act as retarders of oxidation; furthermore, being for the most part precipitated to some degree by polar compounds, they are adsorbed by rubber at the double bonds and thus screen the latter, in this way preventing atmospheric oxidation.

Without such a phenomenon, it would be difficult to understand the mech-

anism of the action of antioxidants which are not in themselves reducing agents, that is, substances which are not oxidized themselves under ordinary conditions; and it would also be difficult to explain why two antioxidants which have different reducing capacities are equally effective protective agents⁸.

It is evident that the activity of alkyl phenols as protective agents in copolymers of butadiene and styrene or acrylonitrile and their vulcanizates varies considerably according to the composition and structure of the alkyl phenol, and the structure determines not only the oxidation capacity, but also the polarity of the molecules.

Some authors⁹ relate the adsorption reaction between rubber and carbon black to the unsaturation of the rubber and the content of volatile substances in carbon black.

If by induction period is understood the time in which the antioxidant, by oxidizing, absorbs oxygen, then, in our opinion, the induction period represents at the same time the period of desorption of antioxidant, after which the segments of a rubber molecule containing double bonds are exposed and subjected to oxidation.

Desorption of the polar molecules of an antioxidant is accelerated by an increase of temperature; hence the induction period is reduced with an increase of temperature. Purified rubber specimens, in which the double bonds are not screened by polar molecules of antioxidant, are characterized by a shorter induction period.

Now we shall present a number of investigations in order to confirm our theory of the mechanism of the inhibiting action of antioxidants on rubber; in this work a group of phenols was studied.

EXPERIMENTAL PART

Regarding antioxidants as polar compounds which, owing to solvation, screen the double bonds of the rubber and thus protect them from oxidation, it was interesting, first of all, to study the simplest case—antioxidants of a chemical nature or those which differ in degree of polarity.

The group of phenols studied included pyrocatechol, resorcinol, hydroquinone, and pyrogallol. Thus, three substances of a single group which differ only in the distribution of the substituent groups and, consequently, in polarity were chosen. The other compound, pyrogallol, contains three substituent groups. It was shown in a series of studies that, in the case of adsorption, too, a strict relation between the adsorption of organic acids and polarity is observed only in acids which are homologous at the substituent groups; other acids, although of like polarity, may deviate from the general rule at the expense of the constituent properties of the molecules.

Antioxidants which are used in industry were chosen for comparison, namely, phenyl-2-naphthylamine (Neozone D) and 2,4-diaminodiphenylamine (Oxyzone).

The constants of the separate antioxidants are listed in Table I.

PREPARATION OF THE RUBBER SOLUTION

Natural rubber was deresinated in an apparatus constructed by B. A. Dogadkin. This apparatus enabled us to separate the resinous substances from rubber in a nitrogen atmosphere. The rubber was deresinated for 28 hours; this gave a pure rubber hydrocarbon to be used in the experiment. Then the rubber was dissolved in benzene and the solution was treated with half-

normal hydrochloric acid to separate the iron salts and then washed with water until no more chlorine was detected in the rubber. The deresinated and purified rubber was coagulated with acetone. The precipitated rubber was again washed with acetone and dried in nitrogen at 40° C.

A 1 per cent solution of rubber in xylene was prepared from the dry rubber. The iron in this solution was measured colorimetrically. The quantity of iron in the given solution was 0.0034 per cent of the rubber. The rubber solution not washed in hydrochloric acid contained 0.00116 per cent iron.

OXIDATION OF RUBBER IN SOLUTION

The rubber-xylene solution was oxidized by a current of air at 100° C. Fifty ml. of the deresinated and purified 1 per cent rubber-xylene solution was poured into a three-necked vessel with ground stoppers (one stopper for the condenser, another for admitting air, and the third for removing the specimens). The vessel with the solution was placed in a water bath at 100° C. Air which had been filtered through concentrated sulfuric acid and columns of calcium

TABLE I
CONSTANTS OF THE ANTIOXIDANTS TESTED

Compound	Melting point (° C)	Boiling point (° C)	Dissociation constant 20-25° C (K)	Solubility (g/100 ml. H ₂ O) at 20° C)	$\alpha \times 10^{16}$
Pyrocatechol	105	245°	4×10^{-10}	45	2.16
Resorcinol	110	281°	4×10^{-10}	123	—
Hydroquinone	170	—	1×10^{-10}	8	2.45
Pyrogallol	133	309°	1×10^{-7}	62	—
Phenyl-2-naphthylamine (Neozone D)	108	395-399.5°	—	—	—
2,4-Diamine-diphenylamine (Oxynone)	130	—	—	—	—
Cresols	—	190-200°	—	—	—
Xylenols	—	200-220°	—	—	—
2-Naphthol	122	286°	—	hardly soluble	1.3

chloride entered the rubber solution from a gasometer at a constant rate of 1 liter per hour. From the column of calcium chloride the air entered a reservoir, and from there it passed to a flask filled with pure xylene heated to 100° (so that the air would not cool the solution and draw the xylene fumes from it).

The dry warm air entered the rubber-xylene solution from the flask of xylene in a constant flow. Oxidation of the rubber was controlled by measuring the relative viscosity of the rubber solution before and during the experiment. During oxidation at certain intervals, the rubber specimens were removed from the xylene solution, and chilled to 20° C; then their relative viscosity was measured in an Ostwald viscometer. In the experiments where the rubber solution was oxidized in the presence of iron palmitate (iron plus palmitic acid) or antioxidants, or in the simultaneous presence of iron palmitate and antioxidants, corresponding doses of these substances were added to the rubber solution at the beginning of the experiment.

OXIDATION OF A RUBBER SOLUTION IN THE PRESENCE OF PHENOLS

The above-mentioned antioxidants were added to a 1 per cent solution of rubber in xylene at the beginning of the experiment. The rubber solution was oxidized by atmospheric oxygen for 6 hours, and in certain cases for 11 hours.

The degree of oxidation of the rubber in solution was manifest by a change of the viscosity of the solutions. The specimens were removed for the first measurement of viscosity a half hour after the experiment began, and then every hour.

In order to determine the effectiveness of the given phenols, the original rubber solution without added antioxidants was oxidized at the same time. The experimental results are presented in Table 2.

The data in Table 2 show the relative viscosities of the rubber solutions after heating at 100°, both with and without antioxidants. A one per cent rubber solution heated without antioxidants loses from 84 to 88 per cent of its initial viscosity even during the first 30 minutes, and 95-96 per cent during 6 hours. Antioxidants retard the decrease in relative viscosity of rubber solutions. However, the antioxidants used do not entirely stabilize rubber in solution. A fall in relative viscosity is still observed, although it is much lower than in the case of oxidation of the original solution without additives. Thus, in the presence of pyrogallol, the viscosity of the original solution after 30

TABLE 2
INFLUENCE OF ANTIOXIDANTS ON THE OXIDATION OF A 1 PER CENT
SOLUTION OF NATURAL RUBBER IN BENZENE AT 100° C
(ACCORDING TO DATA OF RELATIVE VISCOSITY, WHICH
FOR THE INITIAL SOLUTION WAS 32.81)

Time of heating (hours)	Original solution	Original solution with antioxidants						
		Neozone D	Oxynone	Pyrocatechol	Pyrogallol	2-Naphthol	Hydroquinone	Resorcinol
0.5	4.10	17.77	18.07	21.19	21.32	16.64	18.52	7.95
1	2.75	14.07	15.71	16.13	17.95	13.46	15.64	5.90
2	1.90	9.93	14.56	10.90	—	9.48	13.46	4.08
3	1.61	8.81	14.01	8.65	11.87	7.62	11.87	3.21
4	1.43	6.65	13.59	7.05	—	6.19	10.89	2.67
5	1.37	5.78	13.27	6.25	9.8	5.76	9.61	2.34
6	—	—	—	—	8.24	5.06	—	2.07

minutes of oxidation falls 38-45 per cent and in 6 hours, 69-75 per cent. It is possible that destruction of rubber in solution is caused in part by thermal dis-aggregation, as well as by oxidants. The best antioxidants, according to total effectiveness (given by the relative viscosity), are the following: pyrogallol, Oxynone, hydroquinone and pyrocatechol. The inhibiting effect of Neozone-D is weaker than that of the others. Resorcinol is a weak antioxidant.

If the reducing capacity of the phenols studied is compared, then the most effective is pyrogallol which, as is known, is widely used in gas analysis as a good absorber of oxygen in an alkaline medium and as a photographic developer. The next best is hydroquinone, also used as a photographic developer.

Resorcinol and pyrocatechol are less active reducers. It is possible that the reducing capacity of pyrocatechol is reduced by the appearance of an ortho-effect or the mutual influence of OH-groups distributed through the hydrogen bond.

Although the classification of the total effect of the phenol compounds corresponds to their individual oxidation capacity, the extent of total effect does not entirely correspond to the degree of their individual oxidation capacity. In fact, pyrogallol, the most easily oxidized substance, protects rubber from aging somewhat less than does hydroquinone, and only a little less than does

pyrocatechol. Resorcinol differs considerably from all the other phenols, since it has practically no antioxidation effect.

The dissociation constants of the phenols are not an index of their total effect on rubber aging, since pyrocatechol, hydroquinone, and resorcinol, which have different total effects on rubber oxidation, have the same dissociation constant, equal to 4×10^{-10} , while pyrogallol, which protects rubber as well as does hydroquinone, has a much larger dissociation constant, equal to 1×10^{-7} .

In contradistinction to the other derivatives of benzene, which have the same substituent groups in *para*-position and are marked by a dipolar moment = 0, hydroquinone has $\mu = 2.45 \times 10^{-18}$, that is, near to the dihydroxyphenol, pyrocatechol, ($\mu = 2.16 \times 10^{-18}$) in which, however, the OH groups are in *ortho*-position.

The phenols studied, possessing at the same time an oxidation capacity and a certain degree of polarity, can not give a clear picture of the relation between polarity and inhibiting effect, but the fact that two dihydroxyphenols with different oxidation capacities are almost equally effective against the aging of rubber suggests the importance of the polarity of the molecules.

TABLE 3
INFLUENCE OF PEAT PHENOLS ON THE OXIDATION OF A 1 PER CENT
SOLUTION OF RUBBER IN XYLENE BASED ON THE
RELATIVE VISCOSITY

Experiment no.	Time of heating (hours at 100° C)	Relative viscosity				Remarks
		1 per cent cresol fraction	1 per cent xylene fraction	1 per cent Neozone D	No additive	
1	0.5	9.93	9.59	11.36	3.89	Relative viscosity of original solution 19.75
2	1	7.92	7.42	8.85	2.92	
3	2	5.29	4.92	5.77	1.87	
4	3	3.94	3.72	4.53	1.46	
5	4	3.00	3.06	3.89	1.39	
6	5	2.54	2.65	3.23	1.26	

We studied substances of varying polarity which were more stable with respect to oxygen. These experiments disclose a direct relation between the molecularity and inhibiting effect in antioxidants.

INFLUENCE OF PEAT PHENOLS

The water fractions of peat phenols, prepared in the chemical laboratory of the Peat Institute of the Academy of Sciences of White Russia S.S.R., were used as antioxidants. The cresol fraction had a boiling point of 190–200° and the xylene, about 220°. As the data in Table 3 show, the addition of peat phenol fractions to rubber solutions in doses of 1–2 retards the oxidation of rubber. However, the inhibiting effect of peat phenols is somewhat lower than that of Neozone D.

Comparing the antioxidation capacity with the substituents in the phenol compounds, it is seen that, for the substances studied, the antioxidation capacity increases with an increase of hydroxy groups. This may explain the fact that the phenol fractions of coniferous resins, which contain pyrocatechol and other dihydroxyphenols, are more active protective agents for rubber than the phenol fraction of peat resin, where a large part of the phenols are monohydroxyphenols.

TABLE 4
STRUCTURE VISCOSITY OF 1 PER CENT RUBBER SOLUTIONS PREPARED FROM FILMS STORED
IN AIR IN DARKNESS WITH AND WITHOUT ANTIOXIDANTS

Vis- cos- ity of origi- nal solu- tion	Without antioxidant			Pyrocatechol			2-Naphthol			Hydroquinone			Phenol			Pyrogallol		
	40	100	250	400	40	100	250	400	40	100	250	400	40	100	250	400	40*	40**
	Storage time in days																	
20	73.11	25.9	10.4	2.9	Insoluble	72.9	71.8	71.4	71.0	68.4	62.7	70.9	71.3	72.1	35.9	8.5	1.09	Insoluble
30	59.36	22.8	9.5	2.8	Film,	58.3	58.6	58.3	58.2	56.1	49.2	58.1	58.3	58.4	31.1	7.9	1.06	Film
40	51.12	21.2	9.3	2.7	crystalline	52.4	52.0	52.1	50.9	49.8	44.1	50.8	52.3	52.0	28.8	7.7	1.08	68.4 64.2 dissolving
50	45.60	19.3	8.5	2.6	deposit	45.0	44.8	45.7	43.4	43.2	38.3	43.4	44.1	44.7	25.9	7.2	1.10	61.2 56.7 for 2 months, slightly
60	39.26	17.4	7.9	2.5		38.7	38.7	39.8	37.5	38.0	32.7	37.6	39.3	39.1	23.2	6.7	1.07	53.4 49.6 solution
70	35.75	16.5	7.8	2.4		35.2	36.0	36.2	34.2	34.0	29.1	33.8	35.0	36.1	26.1	6.6	1.06	46.4 42.9 would
80	31.09	15.1	7.3	2.4		31.7	31.6	32.1	30.0	30.3	26.9	39.7	32.4	31.9	19.7	6.0	1.08	42.0 38.9 not pass
90	29.06	14.2	7.2	2.3		28.8	29.1	30.0	27.7	27.8	24.1	27.5	28.8	29.4	18.5	5.9	1.06	37.2 34.6 through
																		33.9 32.1 capillary

* The rubber film containing pyrogallol was dissolved in benzene for 25 days before the structure viscosity was measured.

** The second film containing pyrogallol was dissolved 32 days before the structure viscosity was measured.

OXIDATION OF NATURAL-RUBBER FILMS BY ATMOSPHERIC OXYGEN ACCORDING TO DATA OF STRUCTURAL VISCOSITY

We studied the oxidation by atmospheric oxygen of thin rubber films, as well as xylene solutions.

The thin rubber films were prepared by evaporating 25 mm. of a 1 per cent solution of benzene and rubber at 40° on the inner walls of a flask. The relation between the surface area and the amount of rubber in the films was 0.25 g. per 50 sq. cm. of surface. Antioxidants (pyrocatechol, 2-naphthol, pyrogallol, hydroquinone, phenol) were added to the benzene solution in doses of 1 per cent (of the rubber).

The films were kept in darkness in air for 400 days. Changes observed in the films caused by oxidation of the rubber were controlled by measuring the structure viscosity of the benzene solutions.

In order to measure the structure viscosity of rubber films after 40, 100, 250, and 400 days in storage, they were dissolved in the same quantity of benzene as was evaporated earlier (25 ml.). The rubber films were dissolved at 20° C for 48 hours, and then the structure viscosity of the prepared 1 per cent benzene solutions was measured by an Ostwald viscometer (for volatile substances) at the same temperature (Table 4). The structure viscosity of the original 1 per cent rubber solution which was used in preparing the sheets was measured first.

The data in Table 4 show that the structure viscosity of rubber solutions prepared from films which have been stored without antioxidants falls sharply after 40 days and almost disappears after 250 days.

Phenol only slightly retards aging in rubber films.—The structure viscosity of rubber solutions prepared from sheets containing a phenol falls on storage as sharply as that of a solution without antioxidants.

Pyrocatechol and hydroquinone retard the aging of films for 400 days. Changes of the structural viscosity of solutions prepared from films containing 2-naphthol are negligible.

However, films containing pyrocatechol and hydroquinone and stored for 400 days no longer dissolve readily in benzene.

Rubber films containing pyrogallol are particularly insoluble. A solution prepared from a film containing pyrogallol, kept in darkness 40 days, had a high structure viscosity, although solution continued for 25 days. A 1 per cent rubber solution prepared from the same film after 32 days had a lower structure viscosity, although higher than that of the original solution.

A pure natural-rubber hydrocarbon (deresinated) prepared from kok-saghyz does not differ from other types of natural rubber, as earlier studies¹⁰ as well as the work of other authors have shown.

CONCLUSIONS

Oxidation of natural rubber in solution by atmospheric oxygen at 100° C in the presence of antioxidants and iron palmitate was studied. On the basis of the relative viscosity of the oxidized rubber solutions, the following conclusions can be drawn.

1. Addition of 1 per cent of certain antioxidants (pyrogallol, pyrocatechol, hydroquinone, 2-naphthol, resorcinol, Neozone D, and Oxynone) retards the oxidation of rubber in solution. However, this quality of antioxidant is not sufficient to stabilize the solution.

2. Comparison of the effectiveness of antioxidants (according to the data of relative viscosity) showed that the best antioxidant is pyrogallol, followed by pyrocatechol, hydroquinone, and Oxynone. The weakest are Neozone D and especially resorcinol.

3. Pyrogallol A, which is not shown in the table, does not protect a 1 per cent rubber solution from deterioration, showing a relative viscosity in solution of 4.08 at the beginning of the experiment and 1.40 after 7 hours, which is equal to that of the unprotected rubber solution.

4. The cresol and xylenol fractions of peat phenols were also used as antioxidants. The addition of 1 per cent of peat fractions to a rubber solution reduces the drop in relative viscosity of oxidized solutions, but less than does the standard antioxidant, Neozone D.

5. The structure viscosity of solutions prepared from natural-rubber films which were stored 400 days, both with and without antioxidants, was measured.

6. Antioxidants of the phenol type protect rubber during storage in the form of films in darkness in air; in this case the best antioxidant is pyrogallol, and the next best pyrocatechol. 2-Naphthol is more active than hydroquinone.

7. When rubber is stored for a long time in air in darkness in the presence of certain antioxidants of the phenol type, its solubility decreases considerably; this shows the polymerizing action of some phenols on rubber.

8. Pyrogallol has a particularly strong polymerizing effect on rubber films. After 40 days of storage in air, these films dissolve in benzene in 25-30 days; if they are stored longer, their solubility is still less.

REFERENCES

- ¹ Dogadkin and Panchankov, *Zhur. Obshchei Khim.*, **4**, 4 (1944); Dogadkin and Sobaleva, "Khimia fizika-khimia vysokamal. zluh.", Akad. Nauk SSSR, 1952, p. 108.
- ² Kuzminskii and Lazhnev, "Khimia i fizika-khimia vysokamal. zluh.", Akad. Nauk SSSR, 1952, p. 90.
- ³ Yarmolenko, "Khimia i fizika-khimia vysokamal. zluh.", Akad. Nauk SSSR, 1952, p. 182.
- ⁴ Dogadkin, "Khimia i Fizika Kauchuka", 1947.
- ⁵ Kuzminskii, Degetrova, and Laptiova, "Daeledavanni u galine vysokamal. zluh.", Akad. Nauk SSSR, 1949.
- ⁶ Margarytov, "Fizika-khimia kauchuka i gummy", 1941, p. 24.
- ⁷ Garner, Porritt, and Bailey, "Tozmozhenie khimichnykh reaktsii" (Russian translation), 1940, p. 244.
- ⁸ Kitchen and Albert, *Ind. Eng. Chem.*, **42**, 675 (1950).
- ⁹ Polley, Schaeffer, and Smith, *J. Phys. & Colloid Chem.*, **54**, 227 (1950).
- ¹⁰ Yarmolenko and Novikova, *Vesti Akad. Nauk Belarus. SSR*, 1948, p. 117.

STUDY OF THE MECHANISM OF VULCANIZATION OF RUBBER BY MEANS OF RADIOACTIVE SULFUR. II *

S. E. BRESLER, V. P. KUSHNER, AND SAMINSKIĬ

In the first article of this series¹, experimental results of the measurement of diffusion of dissolved (free) sulfur in rubber, and the kinetics of isotopic exchange of vulcanization accelerator (tetramethylthiuram disulfide) with sulfur were reported. A sequence of separate elementary processes which constitute rubber vulcanization was observed in our experiments. In the present study, new experimental results which confirm the individual assumptions made in the first one are presented.

STUDY OF THE MOBILITY OF POLYSULFIDE SULFUR IN VULCANIZED RUBBER AND MEASUREMENT OF THE AMOUNT PRESENT

In the first work¹ it was shown that, during the vulcanization of natural rubber, a secondary combination of sulfur with the rubber is observed at the points where the primary reaction between the sulfur radicals and the chains of the polymer has already taken place. A similar conclusion can be drawn from the peculiar kinetics of sulfur combination in the presence of sufficiently large concentrations (3-5 per cent). In polybutadiene rubber, this phenomenon was hardly observed. We considered it as the formation of polysulfide (length 10-20 S atoms) bridges or cross-links between the natural rubber chains. If this general idea is correct, one would expect such polysulfide bridges to be capable of reversible dissociation corresponding to an increase of temperature.

In fact, the energy of rupture of the polysulfide bond, which is known from a number of thermodynamic data², amounts to $27,000 \pm 5000$ cal. per mole.

If a polysulfide bridge is dissociated, two bonds are broken, but closing of the S_8 ring leads to restoration of one bond. Consequently, thermal dissociation of a polysulfide bridge requires 27,000 cal. per mole. With such a comparatively low dissociation energy of the polysulfide bridge, one would expect to find a uniform concentration of dissociated bridges converted into molecules of free sulfur, principally stable S_8 molecules, at 100-200°. At the points on the polymer chains where this reversible dissociation has taken place, sulfur atoms must be left with unsaturated bonds, that is, having the properties of free radicals. At these "vacancies", migrant free sulfur particles can combine, forming bridges, which are then dissociated, migrating further to new "vacancies", etc.

Hence one would expect that, in vulcanized natural rubber, so-called bound sulfur is to a large degree capable of transfer at normal experimental temperatures. The mobility of bound sulfur, if it is actually due to chemical dissociation of the polysulfide chains and their absorption at other "vacancies", can be called "chemical diffusion". The coefficient of this chemical diffusion must be much smaller than that of the diffusion of free dissolved sulfur molecules. Furthermore, the energy of activation of this chemical diffusion must be related

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to the energy of dissociation of the polysulfide bonds, which has been discussed above.

We set up experiments to measure the mobility or the coefficient of diffusion of chemically bound sulfur in vulcanizates at various temperatures. These experiments, as will be shown later, (1) fully confirmed the mobility of a large part of the chemically bound sulfur in vulcanized natural rubber; (2) confirmed the mechanism of "chemical diffusion", which is due to reversible dissociation and recombination of the chemically bound sulfur; (3) made possible quantitative study of this process by calculating the corresponding diffusion for a simple model which presents the principal features of the system studied in the experiment; and (4) showed that the activating energy of chemical diffusion, as found experimentally, corresponds to the energy of rupture of a polysulfide bridge.

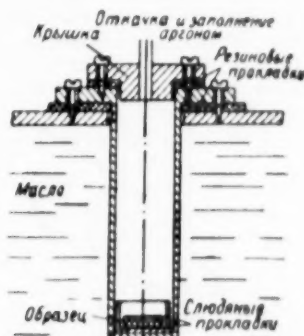


FIG. 1.—Apparatus for studying the diffusion of bound sulfur. The legend at the top center indicates exhausting and charging with argon; that at the top left, cover; that at the top right, rubber gaskets; that at center left, oil; that at bottom left, the test specimen; that at bottom right, mica shield.

EXPERIMENTAL METHODS AND FACTS WHICH CONFIRM THE MECHANISM OF CHEMICAL DIFFUSION OF BOUND SULFUR

The apparatus in which the diffusion of bound sulfur was studied is pictured in Figure 1. In general, it resembles that used in the preceding study¹. There are, however, a few characteristic differences. The measurements of the diffusion of bound sulfur often last 5–10 hours, at 150° and above. Under these conditions it is necessary to protect the specimens from the destructive action of oxygen. In order to avoid oxidation, the apparatus in which the specimens were kept and which, as before, was immersed in oil in an ultrathermostatic oven, was provided with a hermetic cover. When the specimen was put in the apparatus and the cover was screwed on, the interior was evacuated with a vacuum pump and filled with pure argon to a pressure of 1.5 atm. The oxygen in the argon did not exceed 0.1 per cent.

The experiment was performed as follows. Specimens of natural rubber vulcanized by radioactive sulfur S^{35} were prepared. The usual vulcanization recipe was used: 100 parts by weight of rubber, 2 parts sulfur, 0.2 part thiuram, 3.0 parts ZnO ; vulcanization temperature 138° C, time 10 minutes; the specific radioactivity of the sulfur used for vulcanization was 0.2 millicurie per gram.

Sheets 1 mm. thick, from which round specimens 25 mm. in diameter had been cut out, were vulcanized. Before the experiment, it was necessary to eliminate the free sulfur which did not react with the rubber. For this purpose

the specimens were extracted with acetone for a week at room temperature. As will be seen from the results, this method of treating the specimens eliminates free dissolved sulfur almost completely.

The saponified and dried specimens were covered with a sheet of rubber, unvulcanized or vulcanized by ordinary non-radioactive sulfur. The upper layer of rubber served as an acceptor in which diffusion of the radioactive sulfur from the lower layer took place. The thickness of this upper layer was sufficiently large (0.2–0.3 mm.) to absorb all the β -particles released by the lower radioactive specimen.

In order to assure that the lower layer, from which diffusion proceeds, and the upper one into which diffusion takes place were closely fitted together, they were fastened with a thin film of rubber cement. Special experiments showed that the results of the measurements do not depend to any large degree on the amount of rubber cement with which the sheets are fastened. The two-layered specimen thus prepared was placed in the apparatus described above. Radio-

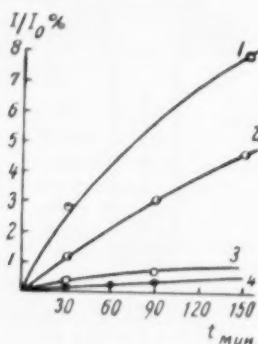


Fig. 2.—Chemical diffusion in unvulcanized and vulcanized rubber films (natural rubber and polybutadiene).

activity in the upper surface of the specimen was measured every hour; for this purpose the specimen was removed from the apparatus and measured by an ordinary *face counter* under standard geometric conditions. Then the specimen was again placed in the heated apparatus and the latter was rapidly evacuated and filled with argon.

The experiments described here, in view of their nature (inert medium), could not be made without removing the specimens from the thermostatic oven as was done for the measurements in the first part of this study.

However, this did not involve great error, since, as special control experiments showed, the temperature of the specimens was established within 2–3 minutes after they were inserted in the heated apparatus. For this reason, the error in the diffusion time applied was not more than 2 per cent. When a specimen was taken out, it cooled very quickly and chemical diffusion stopped altogether.

During these experiments, the appearance of the specimens did not change even after heating for 10 hours at 150° C. When they were heated in air instead of an inert gas, surface destruction was observed within one or two hours.

We shall now discuss the most important qualitative results which directly confirm the mechanism of chemical diffusion described above.

The most important fact is that the amount of radioactive sulfur diffused in the upper layer was large only when this upper layer (the acceptor of the diffused sulfur) was vulcanized rubber. If the upper layer is unvulcanized rubber, only a small quantity of radioactive sulfur will penetrate it. These seemingly paradoxical results were verified several times with various vulcanized and unvulcanized rubbers. The data from several experiments are shown in Figure 2. Curve 3 describes the diffusion of bound sulfur in a layer of unvulcanized natural rubber, curve 1 a vulcanized natural rubber, curve 4 synthetic polybutadiene, and curve 2 vulcanized polybutadiene.

It is important to note that the vulcanized specimens which were used in the upper layer were prepared from the same vulcanization recipes as the vulcanizates in the lower layers, but not with radioactive sulfur.

These experiments can be interpreted only by the theory of chemical diffusion.

In fact, if the upper layer which serves as an acceptor is vulcanized, chemical diffusion must continue until all the mobile radioactive sulfur is distributed uniformly throughout the combined specimen, that is, when the concentration is equal in upper and lower layers, since both layers contain an equal number of sulfur groups subject to reversible heat diffusion in a unit volume.

The fact that, in the case of vulcanized polybutadiene, the amount of diffused sulfur is much less than in the case of natural rubber shows that, in polybutadiene, there is much less mobile or polysulfide sulfur; this is in accord with the data presented earlier¹. When the upper layer (acceptor) is not vulcanized, it contains no sulfur bridges which can be substituted for the radioactive sulfur. Only a small quantity of sulfur can penetrate the unvulcanized rubber according to the uniform distribution of free sulfur formed as a result of reversible dissociation of the bridges in the lower layer.

In the upper layer, the maximum concentration of radioactive sulfur is equal to the uniform concentration of free, that is, dissociated sulfur formed at a given temperature.

QUANTITATIVE STUDY OF THE DIFFUSION OF BOUND SULFUR

We shall now derive a basic differential equation which describes the migration of bound (polysulfide) sulfur, and also the limiting conditions. We shall regard the chemical equilibrium between the polysulfide sulfur bound in the vulcanizate and the dissociated sulfur as being established instantaneously and the rate of the migration of sulfur as being determined by the diffusion of that part of the sulfur which occurs in the free state.

If u'' stands for the concentration of free or dissociated sulfur in a vulcanizate and u' the concentration of bound polysulfide sulfur, chemical equilibrium can be described as follows:

$$u'' = \beta u'$$

where β is the degree of dissociation of the polysulfide bridges.

The difference in the diffusion flow of sulfur will be studied through the element of volume dV for the time dt . As is known from the theory of diffusion, this flow can be written in the form:

$$D \cdot \frac{\partial^2 u''}{\partial x^2} \cdot dV dt$$

where D is the coefficient of diffusion of free sulfur, studied in detail by the authors¹. This quantity of free sulfur is introduced into the element of volume

dV by means of diffusion. Most of it is bound in this volume, that is, it is transformed from free sulfur into bound sulfur. This is due to the fact that the constant of dissociation β is small with respect to unity.

Consequently, it is possible to write the equation:

$$\frac{\partial u'}{\partial t} dV \cdot dt = D \cdot \frac{\partial^2 u''}{\partial x^2} \cdot dV \cdot dt$$

or, using the relation between u'' and u' , we obtain finally

$$\frac{\partial u'}{\partial t} = \beta \cdot D \cdot \frac{\partial^2 u'}{\partial x^2}$$

This is the equation of "chemical diffusion". Formally it coincides with Fick's equation, but in it the effective coefficient of diffusion is $D' = \beta \cdot D$, that is, the product of the true coefficient of diffusion of free sulfur and the degree of dissociation.

In order to formulate the boundary and initial conditions, we must turn to Figure 3, in which our two-layered specimen is depicted.

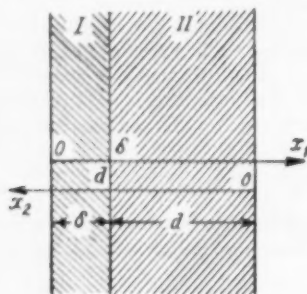


Fig. 3.

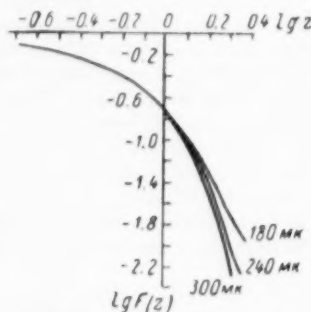


Fig. 4.—Theoretical curve of diffusion from vulcanizate to film.

It is evident that we have two regions with equal constants of effective diffusion D' .

We can describe both regions:

Region I	Region II
$\frac{\partial u'_1}{\partial t} = D' \frac{\partial^2 u'_1}{\partial x_1^2}$	$\frac{\partial u'_2}{\partial t} = D' \frac{\partial^2 u'_2}{\partial x_2^2}$

Initial conditions

$$u'_1|_{t=0} = 0; \quad u'_2|_{t=0} = C_0.$$

Border conditions

$$\begin{aligned} \left. \frac{\partial u'_1}{\partial x_1} \right|_{x_1=0} &= 0; & \left. \frac{\partial u'_2}{\partial x_2} \right|_{x_2=0} &= 0, \\ \left. \frac{\partial u'_1}{\partial x_1} \right|_{x_1=\delta} &= - \left. \frac{\partial u'_2}{\partial x_2} \right|_{x_2=\delta}, \\ u'_1|_{x_1=\delta} &= u'_2|_{x_2=\delta}. \end{aligned}$$

The integral of the equation of diffusion under the initial and boundary conditions indicated has the following form (a detailed solution of the problem is given in the mathematical appendix at the end of the article).

$$u'_1 = \frac{1}{2} C_0 \left\{ \left[1 - \Phi \left(\frac{\delta - x}{2\sqrt{D't}} \right) \right] + \left[1 - \Phi \left(\frac{\delta + x}{2\sqrt{D't}} \right) \right] \right\},$$

where

$$\Phi(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-y^2} dy$$

is the integral of probability; C_0 is the initial concentration of free sulfur before dissociation in the specimen. It is important to note that by no means all the bound sulfur can migrate as a result of heat dissociation. Part of the sulfur (for example, that directly bound with carbon or that which reacts with zinc oxide) undoubtedly can not be mobile at the temperatures studied. For this reason, it is necessary to introduce the coefficient: $k = C_0/C_{\text{total}}$, where C_{total} is the total concentration of sulfur in the specimen (after it is extracted from the non-active sulfur with acetone).

We measured experimentally not the concentration of sulfur, but the activity, which depends on the value of μ (the coefficient of absorption β of the particles in the vulcanizate), as well as on the concentration. The activity I measured during the experiment, related to the initial activity I_0 , which takes place before the attachment of the film to the specimen, is expressed by the following equation:

$$\frac{I}{I_0} = kF(z) \text{ where } z = \frac{\delta}{2\sqrt{D't}}, \text{ the coefficient } K = \frac{C_0}{C_{\text{total}}}$$

and $F(z)$ is the calculated function (see Figure 4) depending on the parameter μ . The theoretical curve I/I_0 , constructed in logarithmic coordinates, is shown in Figure 4. (The value of $\lg F(z)$ is plotted along the ordinates and $\lg z$ along the abscissa.) The thickness of the attached sheet enters not only the factor z , but also as a parameter in the expression for the function $F(z)$. For this reason we calculated and plotted data for three thicknesses δ (180, 240 and 300 mk). Most of the films used were of about this thickness. Figure 4 shows that the course of the relation: $\lg F(z) = f(\lg z)$ changes very little when the thickness δ is varied within the limits indicated. As was said above, it is necessary to measure μ in order to construct the theoretical curves in Figure 4. For this, we used thin vulcanized films of natural rubber, which were stretched between the counter and the standard preparation of radioactive sulfur. Starting from a rubber film of initial thickness 0.10 mm., it is possible, by stretching, to obtain films 0.2 mm. thick. As is known, with sufficient thickness it is possible to assume $I/I_0 = e^{-\mu x}$ or $\ln(I/I_0) = -\mu x$. In Figure 5 the value $-\lg(I/I_0)$ is plotted as a function of the thickness of the film (the latter was determined by weighing a film of standard area). A linear relation, from which the value $\mu = 333$ (1/cm.) can be determined, is obtained.

The coefficient of absorption μ was measured with the same geometrical arrangement and the same position of the film with respect to the radioactive specimen as in the fundamental experiments. This value was used in all succeeding calculations.

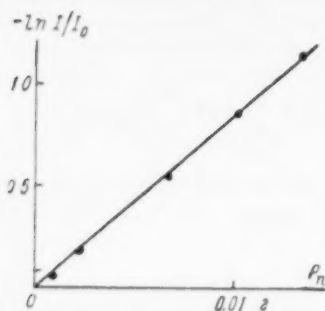


FIG. 5.—Combination of β -particles of S^{22} with rubber.

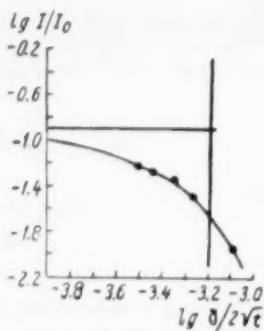


FIG. 6.—Graphic calculation of coefficient of diffusion. Natural rubber, $T = 120^\circ \text{C}$; $\delta = 238 \text{ mk}$.

Now the use of the experimental data in finding the two unknown quantities D' and k will be discussed.

The experiment gave a number of values of the activity I measured on the specimen at various moments.

Furthermore, the value I_0 (the original activity of the lower or thicker specimen without the upper layer) was measured before the experiment. The following curve was constructed in logarithmic coordinates according to the experimental data.

$$\lg \frac{I}{I_0} = f \left(\lg \frac{\delta}{2\sqrt{t}} \right)$$

The scale to which the experimental curve was drawn was chosen just as for the construction of the theoretical curve:

$$\lg F(z) = f \left(\lg \frac{\delta}{2\sqrt{D't}} \right)$$

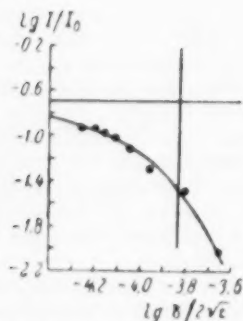


FIG. 7.—Natural rubber, $T = 159^\circ \text{C}$; $\delta = 388 \text{ mk}$.

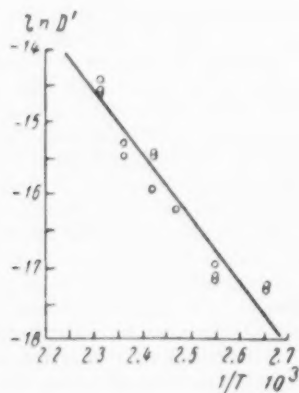


FIG. 8.—Temperature relation of coefficient of chemical diffusion in natural rubber.

It is clear that both curves (theoretical and experimental) have exactly the same form, and can be superimposed by simple parallel transposition of the coordinate axes.

When the curves are superimposed, the abscissa of the beginning of the coordinate of the theoretical curve will be equal to $\lg \sqrt{D'}$, and the ordinate will give the value $\lg k$. Examples of this superimposition of the experimental points on the theoretical curve by parallel transposition of the latter are shown in Figures 6 and 7.

We were convinced that, in all cases, it is possible to perform this operation without any difficulty. The results of measurements of the values k and D' in vulcanized natural and synthetic rubber at various temperatures are shown in Table 1. The values of k are corrected for the quantity of sulfur which reacts with zinc oxide.

TABLE 1
AMOUNT OF POLYSULFIDE SULFUR AND COEFFICIENT
OF "CHEMICAL DIFFUSION"

Temperature (° C)	Natural rubber			Polybutadiene		
	δ (mk)	k (%)	$D' \cdot 10^7$ sq. cm./sec.	δ (mk)	k (%)	$D' \cdot 10^7$ sq. cm./sec.
159	243	40.0	5.25			
	388	36.0	4.05			
	208	39.0	4.80			
151	318	41.0	2.20	241	20.0	1.10
	254	24.5	1.82			
140.5	244	75.5	1.70			
	280	66.5	1.95	289	28.0	0.89
	243	68.5	1.82			
132	244	62.0	0.87	323	23.0	0.72
120	226	63.0	0.325			
	222	59.0	0.415			
	238	43.5	0.340			
104	245	39.0	0.30			
	384	28.0	0.30			

From the table it is seen that the values of k in the various specimens vary slightly; this can be explained by the fact that the specimens were prepared under conditions of commercial vulcanization, and one can not expect complete uniformity.

All these variations of the value of k do not conceal the difference between natural rubber, for which k averages 55, and synthetic polybutadiene, for which $k \approx 20$ per cent. Consequently, the differences found previously in the behavior of both rubbers are confirmed by the data. As for the coefficient of chemical diffusion D' , there is a certain scattering of the figures, but within comparatively narrow limits. This fact, the weak relation between the value of $D' = \beta \cdot D$ obtained experimentally and the variation in vulcanization conditions, is per se a confirmation of the observed picture of chemical diffusion, since the degree of thermal dissociation of polysulfide sulfur changes much less with a change in the total quantity of polysulfide sulfur C_0 than the value k , which is simply proportional to C_0 ($k = C_0/C_{\text{total}}$).

Since the accuracy of the measurement of D' is not too great and the proportional error can be estimated as ± 20 per cent, we plot all the experimental points on the coordinates: $\lg D' = f(1/T^\circ\text{K})$ without introducing any corrections. As is seen from Figure 8, a straight line can be drawn through the experimental point. We did this by the method of least squares, and obtained a value of the activating energy for the value $D' = 17,500 \pm 2500$ cal. per mole. The value of D' as a function of the temperature is expressed by the formula:

$$D' = D'_0 e^{-E/RT} = 250 e^{-17,500/RT}$$

It is evident that if D' is divided into D , which according to our data is $D = 0.006 e^{-7000/RT}$, then $\beta = 4 \cdot 10^4 e^{-10,500/RT}$. Hence at 100°C $\beta = 3\%$, and at 160°C $\beta = 22\%$. These are the experimental values of the degree of dissociation of migrant (polysulfide) sulfur.

DISCUSSION OF THE RESULTS

The experiments described above fully confirm the concept of chemical diffusion of bound sulfur. A particularly convincing fact is the practical absence of this process if sheets of unvulcanized rubber are used as acceptors. The coefficients of chemical diffusion D' , measured under various experimental conditions for films of various thicknesses δ and for various vulcanized specimens coincide sufficiently with a scattering which does not exceed the limits of error ($\pm 20\%$). The relation between the coefficient of chemical diffusion and $1/T$ is exponential, and the energy of activation of the process was equal to $17,500 \pm 2500$ cal. per mole.

We can calculate this value theoretically from the following considerations. According to the laws of chemical equilibrium the constant of equilibrium between dissociated and bound polysulfide sulfur is determined as follows:

$$k_p = \frac{C' C''}{C_0} = A e^{-U/RT}$$

where C_0 is the total concentration of polysulfide sulfur; C' is the concentration of dissociated polysulfide sulfur; C'' is the concentration of vacant places formed during dissociation, and U is the heat of dissociation of a bridge, that is, the energy of rupture of a polysulfide bond.

Since $C'' = aC'$, where a is a constant coefficient, then:

$$C = \sqrt{\frac{AC_0}{a}} e^{-U/RT}$$

consequently

$$\beta = \frac{C'}{C_0} = \sqrt{\frac{A}{aC_0}} e^{-U/2RT}$$

The coefficient of chemical diffusion is $D' = \beta \cdot D$, and D is the coefficient of diffusion of free sulfur.

$$D = D_0 \cdot e^{-U_0/RT}$$

Consequently, D' measured experimentally must depend on the temperature according to the law:

$$D' = D'_0 \cdot e^{-[U_0 + (U/2)]/RT}$$

We know that $U = 7000$ cal. per mole, so that for the energy of diffusion of a polysulfide bond, we obtain $U = (17,500 - 7000)2 = 21,000$ cal. per mole. We must compare this value with that obtained from the thermodynamic data, $27,000 \pm 5000$ cal. per mole. Since our value for U also includes a probable error of 4000–5000 cal. per mole, it is necessary to regard the agreement between the two values as satisfactory. A further precision of both the data on chemical diffusion and the thermochemical data on the energy of dissociation of a polysulfide bond is desirable.

STUDY OF THE CHEMICAL DIFFUSION OF SULFUR IN EBONITE

Ebonite contains about 30 per cent by weight of sulfur in the bound state. One would naturally expect that most of the cross-links in ebonite are polysulfide. It can be assumed that sulfur diffuses through ebonite by the same mechanism of chemical diffusion as in vulcanized rubber.

If a thin layer of radioactive sulfur is applied to the ebonite specimen and heated, the sulfur will begin to diffuse through the specimen. However, the action is not limited to simple diffusion; radioactive sulfur, at first free, will replace the dissociated polysulfide bridges inside the ebonite. At any moment only a part of the radioactive sulfur will remain free and mobile. Consequently, by measuring the coefficient of diffusion of radioactive sulfur applied to an ebonite film, one can again determine χD , where D is the coefficient of diffusion of free molecular sulfur in softened ebonite, χ is the degree of dissociation of the chemically bound bridge sulfur. Unfortunately, the value of D is not known separately. For this reason we can interpret the results only qualitatively by comparing the energy of activation of diffusion with the heat of dissociation of the polysulfide bonds. For comparison, we measured the diffusion of sulfur at the same temperatures in escapone, that is, reinforced rubber which contains no sulfur. In it one would evidently expect an altogether different mechanism of sulfur mobility than in ebonite.

MEASUREMENTS AND CALCULATIONS

In measuring the coefficient of diffusion, we used the absorption of β -particles in ebonite.

The use of this method has been described several times in the literature³. It is possible with it to measure quite low rates of diffusion, since in layers 30 mk. thick more than 60 per cent of the β -particles are absorbed.

A given quantity of radioactive sulfur from a fine suspension of sulfur in alcohol was applied in a thin uniform layer to the surface of a thin film of ebonite or escapone ($x = 0$).

The activity of the applied layer was measured with a counter. Then the specimen coated with sulfur was placed in a thermostatic oven and kept there at a fixed high temperature. Owing to diffusion, the sulfur penetrated into the specimen, and the activity measured on the boundary $x = 0$, under constant geometric conditions, decreased according to the absorption of β -particles in the specimen. The fall of activity in time is an index of the rate of diffusion and, if the coefficient of absorption of β -particles in ebonite and escapone is known, the effective coefficient of diffusion (χD) can be calculated.

At temperatures above 120°C , sulfur is strongly vaporized (vapor pressure is greater than 0.05 mm.). For this reason it is necessary to keep the specimens sealed up. The experiment was carried out as follows. Two identical speci-

mens, prepared by the method described above, were joined so that the sulfur-coated surfaces were pressed together. These specimens were then compressed in a special apparatus and placed in a thermostatic oven for a short time (15–20 minutes at 140° C or 10–15 minutes at 155° C). In this period the sulfur penetrated to some extent into the specimen, but so little that the total activity of both specimens before and after heating was the same. This is proof that the sulfur was concentrated in a thin surface layer, so it is possible to ignore the absorption of β -particles in the latter.

The prepared films were purified of possible residual undissolved sulfur by abrasion of the surface layer with a fine emery cloth.

The specimen containing radioactive sulfur in a very thin surface layer was placed in the apparatus (Figure 9). In order to exclude the possibility of evaporation of sulfur from the surface, the surface was covered with a thin (10–15 mk.) sheet of mica; the cover of the apparatus pressed the mica tight against the specimen.

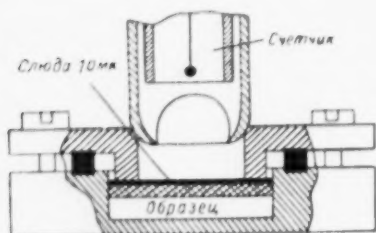


Fig. 9.—Apparatus for studying chemical diffusion in ebonite. The legend at top left indicates mica shield; that at top right, counter; that at bottom center, test-specimen.

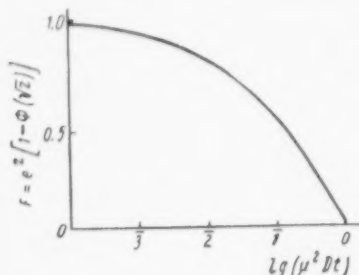


Fig. 10.—Theoretical curve of chemical diffusion in ebonite.

After the specimen was mounted in the apparatus, its initial activity I_0 was measured. Then the apparatus and a high-temperature counter were put in a thermostatic oven. The activity of the specimen was measured at intervals of 15, 30, and 60 minutes.

Since the specimens could be considered semi-infinite bodies, the boundary conditions for them are:

$$C = 0 \quad \text{for} \quad x = \infty$$

and

$$\frac{\partial C}{\partial x} = 0 \quad \text{for} \quad x = 0$$

The initial condition is $C = C_0 \delta(x)$.

The solution of the diffusion equation:

$$\frac{\partial C}{\partial t} = \chi D \frac{\partial^2 C}{\partial x^2}$$

for these boundary and initial conditions is well known.

$$C = \frac{C_0}{\sqrt{\pi \cdot \chi \cdot D \cdot t}} \cdot e^{-x^2/4\chi \cdot D \cdot t}$$

Proceeding to the activity, we obtain:

$$\frac{I(x, t)}{I_0} = \frac{1}{C_0} \int_0^\infty C(x, t) e^{-\mu x} dx$$

where μ is the coefficient of absorption of β -particles in the specimen. By elementary transformations we obtain:

$$F = \frac{I(x, t)}{I_0} = e^z [1 - \Phi(\sqrt{z})]$$

where

$$z = \mu^2 \chi D t \quad \text{and} \quad \Phi(\sqrt{z}) = \frac{2}{\sqrt{\pi}} \int_0^{\sqrt{z}} e^{-y^2} dy$$

Gauss' integral of probabilities from the factor \sqrt{z} .

In treating the experimental data, we shall also use the earlier graphic method.

At constant temperature, the value of z is a function of the time alone, since μ and χD are constants. Furthermore:

$$\lg z = \lg (\mu^2 \chi D) + \lg t.$$

Constructing the theoretical curve $F = f(\lg z)$ (Figure 10) and plotting the experimental relation: $F = f(\lg t)$, on the same scale, we obtain two uniform curves, which are displaced along the abscissas to a constant value of $\lg (\mu^2 \cdot \chi D)$. Shifting one curve with respect to the other, we cause both curves to be displaced.

Thus we obtain, first, a criterion for determining the validity of our experiments, since the experimental points must lie on the theoretical curve, and, second, the possibility of calculating the coefficient of diffusion according to the degree of displacement, equal to $\lg (\mu^2 \cdot \chi D)$.

EXPERIMENTAL RESULTS AND DISCUSSION

The results of an experiment made at 125° are shown in Figure 11.

It is seen that the theoretical curve passes through the experimental points for two independent experiments; the displacement in this case is 6.94, hence the coefficient of diffusion is:

$$\chi \cdot D = 0.8 \cdot 10^{-10} \text{ cm}^2/\text{sec}.$$

The results of the experiments with ebonite and escapone are shown in Figure 12 in the coordinates $\lg \chi \cdot D$ and $(1/T^\circ \text{ K}) 10^3$.

For ebonite, the coefficient of diffusion can be regarded as a function of the temperature in the equation $\chi \cdot D = 1.2 \times 10^6 e^{-28,900/RT}$, and for escapone $\chi \cdot D = 4 \cdot 10^{15} e^{-55,000/RT}$.

The activating energy of diffusion obtained in ebonite (28,000 cal./mole) corresponds to the value expected on the basis of the theories of chemical diffusion.

In escapone it is evident that the mechanism of sulfur migration is altogether different; this is reflected in the very high activating energy (55,000 cal./mole).

STUDY OF THE REACTION BETWEEN FREE SULFUR RADICALS AND THE RUBBER SURFACE

In the first article it was shown that, in order to explain the observed kinetics of absorption of sulfur by rubber, it is necessary to assume the existence of free sulfur radicals $-S-S-$ in the early stages of the process.

The object of these experiments was to obtain such radicals independently and to prove that they react easily with rubber.

S''_2 radicals can be obtained by heat dissociation of S_8 molecules in vapor form. A molecular cluster of these radicals was obtained in a vacuum, and a rubber specimen was bombarded with them. In these experimental conditions sulfur can be bound only by the surface layer of the rubber, forming in the optimal case a monomolecular film. However, this does not limit our investigations. Using radioactive sulfur S^{35} and radiometry, it is possible to measure quantities of sulfur which constitute scarcely 1 per cent of the monolayer.

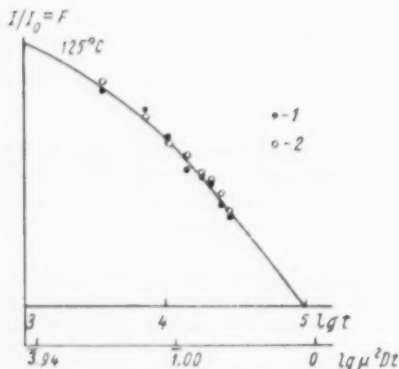


Fig. 11.—Experimental curve for ebonite at 125° C.
1—experiment No. 7; 2—experiment No. 8.

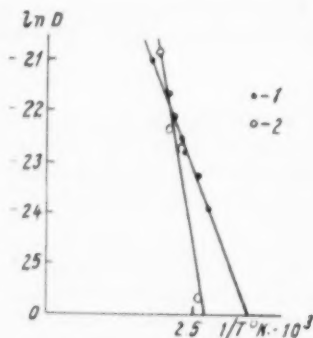


Fig. 12.—Temperature relation of coefficient of diffusion in ebonite and escapone.
1—ebonite; 2—escapone.

DESCRIPTION OF APPARATUS AND METHODS

A "molecular gun", consisting of a glass vessel (Figure 13, 5) of 15 mm. diameter, heated in an oven, and a nozzle (Figure 13, 6) in the form of a capillary of inner diameter 1.3 mm., on which a superheater was wound, was placed in a vacuum apparatus (Figure 13, 1) evacuated to 10^{-4} mm.

Several milligrams of radioactive sulfur was placed in the upper reservoir of the "gun", and it was then sealed. The apparatus contains two thermocouples as well as two ovens. One of the former (Figure 13, 3) measures the temperature in the coldest place—at the bottom of the reservoir, the second (Figure 13, 4) measures the superheating temperature in the nozzle. After a vacuum was obtained in the apparatus, the reservoir with the sulfur was heated by a current to 100–120° C, and the superheater reached a temperature of 300–450° in the nozzle. The rubber specimen (Figure 13, 8) was placed 5 cm. away from the opening of the nozzle.

Uniform equilibrium dissociation in sulfur vapor is well known², and the

concentration of S''_2 radicals at various vapor pressures in the reservoir and at various superheater temperatures can be calculated.

The calculation shows that, when chemical equilibrium is established, the S''_2 radicals constitute 5 per cent of the total sulfur at 300° and 0.01 mm. vapor pressure, and 28 per cent at the same temperature and 0.001 mm. vapor pressure. At 450° C and 0.001–0.1 mm. pressure the radicals are almost 100 per cent.

After the rubber specimen was exposed for 10–20 minutes in the apparatus, the ovens were switched off and the rubber was removed from the vacuum. The activity of the layer of sulfur which covered it was then measured. Next the sulfur was washed off with several doses of acetone for 3–7 days. Control experiments showed that this period is more than enough to eliminate all unreacted sulfur from the specimen.

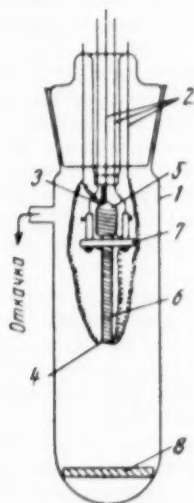


FIG. 13.—Apparatus for obtaining molecular cluster of sulfur radicals.
The legend on the left center indicates the pump.

The specific activity of the sulfur used (0.04 millicurie per mg.) was carefully measured in advance. For this reason, by measuring the activity of the specimens after rinsing, we were able to determine the absolute quantity of bound sulfur on the surface.

EXPERIMENTAL RESULTS AND DISCUSSION

Only the first results obtained by this method can be offered at present. They show beyond doubt that sulfur converted into S''_2 radicals is chemically bound with rubber at room temperature. The fact that the S''_2 radicals, when brought out of the nozzle, have a high temperature is of no importance. The experiment showed that chemical combination also takes place on the underside of the specimen (if it is not specially protected), that is, after the S''_2 molecules have undergone numerous collisions with the wall of the apparatus and have reached the temperature of the wall. If the monomolecular sulfur layer on the

rubber is taken as the basis of all discussions, the amount of sulfur applied to the specimen can be related to the capacity of the monolayer, since it contains $4 \cdot 10^{-8}$ g. per sq. cm. of sulfur, as can be easily demonstrated.

The experiment shows that, at low superheater temperatures (150–200°), much sulfur settles on the specimen. It is easy to obtain a surface deposit which amounts to 200–300 per cent of the monolayer. After rinsing, little activity remains, corresponding to 1–2 per cent of the monolayer, that is, 1/100 to 1/200 of the initial condensed sulfur. If the superheater is heated to 400°, the picture is changed. The total amount of sulfur deposited on the rubber during exposure becomes much smaller, i.e., of the order of 10 per cent of the monolayer, but then, after washing, more than half of it remains in the form of chemically bound sulfur. Consequently, an increase of the concentration of free radicals in a molecular cluster leads to a sharp increase of bound sulfur on the surface. The fact that molecular sulfur did not condense readily in these experiments is explained by the method of heating the rubber specimen by emission from the superheater. In order to improve the conditions for sulfur condensation on the specimen, experiments were made by cooling the flask of the apparatus with liquid air. Under these conditions the specimen remains very cold. This step increased the condensation of sulfur on the surface of the specimen to 80–110 per cent of the monomolecular deposit.

In this case 23 per cent of the monolayer remained on the upper surface of the specimen and 13 per cent on the lower surface after rinsing in acetone. These results leave no doubt that sulfur radicals can attack rubber at room temperature and give by-products of the absorption of sulfur by the hydrocarbon.

When the temperature of the superheater is reduced, the relative concentration of free radicals in the sulfur vapor falls sharply, and the effect of combination of sulfur with the surface layer of the rubber approaches zero, although the surface conditions become much more favorable to condensation of molecular sulfur. The experiments described are qualitative, but we can expect this method to be perfected and developed into a quantitative method.

The formation of S''_2 radicals is the primary process in the reaction between an accelerator and elemental sulfur. In the first article of this series¹, we suggested a possible decomposition of thiuram disulfide into radicals, with separation of two central sulfur atoms. However, an alternative mechanism is also possible. Experiments of A. L. Klebanskiĭ and L. P. Fomina have shown that a labile intermediate substance, thiuram tetrasulfide, is formed during the reaction of thiuram disulfide and organic polysulfides. This substance was isolated and studied. The additional two sulfur atoms in it are not bound in a linear chain as in thiuram disulfide, but appear to be coordinated. They are easily separated, forming a S_2 fragment. All the data presented in the first article fit this scheme. Final selection of the mechanism required more experimental work.

MATHEMATICAL APPENDIX

On page 983 we formulated the fundamental problem of chemical diffusion. It consists in integrating the diffusion equation:

$$\frac{\partial u'}{\partial t} = D' \frac{\partial^2 u'}{\partial x^2}$$

in two parallel layers of a vulcanizate under the initial and boundary conditions stated. The problem was solved by the operation method. Proceeding to the

description of the functions \bar{u}'_1 and \bar{u}'_2 , we obtain for both regions

$$\bar{u}'_1 = \int_0^\infty e^{-p\tau} u'_1 d\tau \quad \bar{u}'_2 = \int_0^\infty e^{-p\tau} u'_2 d\tau,$$

where $\tau = D't$. The equations have the form:

$$\frac{d^2 \bar{u}'_1}{dx_1^2} - p \bar{u}'_1 = 0; \quad \frac{d^2 \bar{u}'_2}{dx_2^2} - p \bar{u}'_2 + C_0 = 0,$$

hence, we obtain for the function described:

$$\begin{aligned} \bar{u}'_1 &= A \operatorname{sh} \sqrt{p} x_1 + B \operatorname{ch} \sqrt{p} x_1, \\ \bar{u}'_2 &= C \operatorname{sh} \sqrt{p} x_2 + D \operatorname{ch} \sqrt{p} x_2. \end{aligned}$$

From the boundary conditions:

$$\left. \frac{d\bar{u}'_1}{dx_1} \right|_{x_1=0} = 0 \quad \left. \frac{d\bar{u}'_2}{dx_2} \right|_{x_2=0} = 0$$

we obtain $A = 0$ and $C = 0$.

From the conditions:

$$\left. \frac{d\bar{u}'_1}{dx_1} \right|_{x_1=\delta} = - \left. \frac{d\bar{u}'_2}{dx_2} \right|_{x_2=d} \quad \bar{u}'_1|_{x_1=\delta} = \bar{u}'_2|_{x_2=d}$$

we obtain:

$$B = \frac{C_0}{p} \frac{\operatorname{sh} \sqrt{p} d}{\operatorname{sh} \sqrt{p} (d + \delta)},$$

hence, finally:

$$\bar{u}'_1 = \frac{C_0 \operatorname{sh} \sqrt{p} d \operatorname{ch} \sqrt{p} x_1}{p \operatorname{sh} \sqrt{p} (d + \delta)}.$$

The value of \bar{u}'_2 will no longer be necessary.

A few algebraic transformations will now be made.

$$\bar{u}'_1 = \frac{C_0 e^{-\sqrt{p}(d+\delta)} [e^{\sqrt{p}(d+x_1)} - e^{-\sqrt{p}(d-x_1)} + e^{\sqrt{p}(d-x_1)} - e^{-\sqrt{p}(d+x_1)}]}{2p [1 - e^{-2\sqrt{p}(d+\delta)}]}$$

but

$$\frac{1}{1 - e^{-2\sqrt{p}(d+\delta)}} = \sum_{n=0}^{\infty} e^{-2n\sqrt{p}(d+\delta)},$$

since

$$|e^{-2\sqrt{p}(d+\delta)}| < 1$$

(if we assume $\operatorname{Re} \sqrt{p} > 0$).

By term multiplication we obtain \bar{u}'_1 in the form of

$$\begin{aligned} \bar{u}'_1 &= \frac{1}{2} C_0 \sum_{n=0}^{\infty} \left\{ \frac{1}{p} e^{-\sqrt{p} [d-x_1+2n(d+\delta)]} + \frac{1}{p} e^{-\sqrt{p} [d+x_1+2n(d+\delta)]} \right. \\ &\quad \left. - \frac{1}{p} e^{-\sqrt{p} [d-x_1+2d+2n(d+\delta)]} - \frac{1}{p} e^{-\sqrt{p} [d+x_1+2d+2n(d+\delta)]} \right\}. \end{aligned}$$

The original of the function u'_1 is found now.

Transformed functions such as $(1/p) \cdot e^{-x'\sqrt{p}}$ are often encountered in problems of mathematical physics. Their primary function is:

$$1 - \Phi\left(\frac{x'}{2\sqrt{t}}\right) = 1 - \Phi\left(\frac{x'}{2\sqrt{D't}}\right),$$

where Φ is the integral of probability,

$$\Phi(\alpha) = \frac{2}{\sqrt{\pi}} \int_0^\alpha e^{-y^2} dy.$$

We can now write the expression of the primary function of:

$$\begin{aligned} u'_1 = \frac{1}{2} C_0 \sum_{n=0}^{\infty} & \left\{ \left[1 - \Phi\left(\frac{\delta - x_1 + 2n(d + \delta)}{2\sqrt{D't}}\right) \right] \right. \\ & + \left[1 - \Phi\left(\frac{\delta + x_1 + 2n(d + \delta)}{2\sqrt{D't}}\right) \right] \\ & - \left[1 - \Phi\left(\frac{\delta - x_1 + 2d + 2n(d + \delta)}{2\sqrt{D't}}\right) \right] \\ & \left. - \left[1 - \Phi\left(\frac{\delta + x_1 + 2d + 2n(d + \delta)}{2\sqrt{D't}}\right) \right] \right\}. \end{aligned}$$

With "brief periods of time" this series converges very rapidly, and when $d \geq 3\delta$ even for $\delta/2\sqrt{D't} = 0.2$, that is, when the time $t = \delta^2/0.16D'$, the error does not exceed 5 per cent if all the members of the series except the first two are discarded.

In our case, $\delta \simeq 10^{-3}$ cm. and $D' \simeq 10^{-8}$ sq. cm. per sec.; hence, the maximum admissible time is $t \simeq 10^8$ sec., that is, about one day.

With shorter experimental times (and they actually were much less than a day long) and, consequently, with large ratios d/δ , the error is considerably less.

Thus we shall use the solution of:

$$u'_1 = \frac{1}{2} C_0 \left\{ \left[1 - \Phi\left(\frac{\delta - x}{2\sqrt{D't}}\right) \right] + \left[1 - \Phi\left(\frac{\delta + x}{2\sqrt{D't}}\right) \right] \right\}.$$

Now we turn to the calculation of the value measured in the experiment, i.e., the activity.

In a layer dx thick lying at a depth x , the quantity of radioactive sulfur under the surface of the film is:

$$u'_1(x)dx$$

The activity of this sulfur, measured by the counter, will decrease $e^{-\mu x}$ times, owing to the absorption of β -particles.

Hence the total activity falling on the counter is:

$$I = a \int_0^\infty u'_1(x) e^{-\mu x} dx,$$

where a is the coefficient of proportionality and μ is the coefficient of combination, equal in our experiments to 333 cm.^{-1} .

Since the films were quite thick, this can be integrated to infinity.

Substituting the solutions obtained for $u_1(x)$ in the subintegral function and integrating, we obtain:

$$I = \frac{a C_0}{\mu} \frac{1}{2} \left\{ 2[1 - \Phi(z)] + e^{-\mu\delta + (\mu^2\delta^2/4z^2)} \left[1 - \Phi\left(\frac{\mu\delta}{2z} - z\right) \right] - e^{\mu\delta + (\mu^2\delta^2/4z^2)} \left[1 - \Phi\left(\frac{\mu\delta}{2z} + z\right) \right] \right\}$$

where $z = \delta/2\sqrt{D't}$.

In order to exclude the constant coefficient a , we measured the activity on the specimen before the experiment before it is covered with the thin rubber film.

This value is:

$$I_0 = \int_0^\infty a C_{\text{total}} e^{-\mu x} dx = \frac{a}{\mu} C_{\text{total}}.$$

Introducing $C_0/C_{\text{total}} = k$, we can finally write the solution of the problem in the form: $I/I_0 = kF(z)$, where

$$F(z) = [1 - \Phi(z)] + \frac{1}{2} \left\{ e^{-\mu\delta + (\mu^2\delta^2/4z^2)} \left[1 - \Phi\left(\frac{\mu\delta}{2z} - z\right) \right] - e^{\mu\delta + (\mu^2\delta^2/4z^2)} \left[1 - \Phi\left(\frac{\mu\delta}{2z} + z\right) \right] \right\}.$$

The function $F(z) = F(\delta/2\sqrt{D't})$ depends on the thickness of the film as well as the parameter.

The function $F(z)$ plotted on logarithmic coordinates, is shown in Figure 4. It was calculated for three thicknesses, δ , 180, 240 and 330 mk.

In calculating the integrals of probability, with the factor $z > 2$, we used the asymptotic expression of these functions:

$$1 - \Phi(z) = \frac{1}{\pi} e^{-z^2} \sum_{n=0}^{\infty} \frac{(-1)^n \Gamma\left(n + \frac{1}{2}\right)}{z^{2n+1}}$$

where $\Gamma(n + \frac{1}{2})$ is a function of the corresponding number.

The experimental data were treated as described above by theoretically calculating $F(z)$.

CONCLUSIONS

The following general conclusions can be made on the basis of the work done.

1. In some rubbers, especially natural rubber, a non-linear absorption of sulfur in large concentrations (over 1 per cent) is observed at sufficiently high temperatures. Deviation from the simple kinetic characteristics of the process can be treated as a superimposition of a secondary process, in which additional sulfur is absorbed at the same points where it is bound with the hydrocarbon, by the primary process of combination between rubber and sulfur. Polysulfide

bridges are formed between the rubber chains. This explains the non-linearity of the total process of absorption of sulfur by rubber.

2. This view of the vulcanization process and the nature of the combination of sulfur under ordinary vulcanization conditions ($S = 1-2$ per cent and $T = 130-140^\circ \text{C}$) is confirmed by direct measurements of the mobility of bound sulfur in vulcanizates. The suggested process of "chemical diffusion" fully explains the observed effects, and makes it possible to calculate the constant of diffusion D' and the amount of polysulfide sulfur in the specimen.

3. The great reactivity of the free S''_2 sulfur radicals, which can react with rubber at room temperature, was proven. This confirms an earlier hypothesis¹ of the action of sulfur biradicals in the vulcanization process.

REFERENCES

- ¹ Bresler, Khaiman, and Pryadilova, *Zhur. Tekh. Fiz.* **24**, 4 (1954).
- ² Powell and Eyring, *J. Am. Chem. Soc.* **65**, 648 (1943).
- ³ Lbov, *Uspekhi Fiz. Nauk* **42**, 409 (1950).
- ⁴ Staigman, Shockly, and Nix, *Phys. Rev.* **63**, 13 (1939).
- ⁵ Bracke, Peter, and Neveling, *Z. Naturforsch.* **6c**, 32 (1951); Gee, *Trans. Faraday Soc.* **48**, 515 (1952).

STUDIES OF MASTICATION *

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Despite notable progress during recent years, there is still much to be elucidated regarding the chemical reactions involved during what might be described as normal mastication. By normal mastication is meant the processing of natural rubber, without additives, on two-roll open mills or in internal mixers, under conditions such that the temperature of the rubber does not exceed 100° to 120° C. It is known that, during such mastications, rubber molecules are mechanically broken, that on an average 0.2 per cent of oxygen combines with the rubber, and that at least some of this oxygen reacts with the free radical ends of the broken rubber chains and prevents their recombination¹.

ACETONE EXTRACT OF MASTICATED RUBBER

It has long been known that the acetone extract of rubber increases during mastication, although the acetone-soluble substances produced have not been investigated².

Sheets of pale crepe, 1.0 to 1.5 mm. thick, were acetone-extracted in a Soxhlet apparatus, in an atmosphere of nitrogen for nine hours. The rubber was then placed in a vacuum-desiccator and the acetone removed from the rubber by passing a current of nitrogen through the desiccator for twenty minutes and then reducing the pressure. Mastications were performed on a two-roll 9 × 4½-inch mill, with the rolls running at a friction ratio of 2:1. The masticated rubber was then acetone-extracted in nitrogen for eight hours, and this second extract was examined.

The small extracts which were obtained after mastication defied analysis by conventional organic chemistry techniques, so recourse was made to infrared spectroscopic measurements³.

An extract obtained after rubber had been milled on rolls at 20° C for fifteen minutes amounted to 0.139 per cent of the rubber used. Its infrared spectrum was traced and included absorption bands at 840 and 890 cm^{-1} . The trisubstituted ethylenic double bond group absorbs at 840 cm^{-1} , and bands at 840 and 890 cm^{-1} appear in the spectrum of natural rubber⁴. A further quantity of rubber was given the same treatment except that it was not milled between extractions and the second extract (amounting to 0.036 per cent) did not show infrared absorption bands at these two frequencies. These bands were also absent from the spectrum of the original nine-hour acetone extract of rubber.

The materials producing the absorption bands at 840 and 890 cm^{-1} did not emanate from the protein present in the pale crepe, nor from the acetone used for the extractions, since similar results were obtained using either deproteinized pale crepe rubber or using methyl alcohol as the extractant.

The extract obtained after fifteen minutes' cold milling was fractionated by

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chromatographic analysis, using an aluminum oxide column. Five fractions were obtained:

A. Insoluble in benzene	8.7
B. A benzene eluate	20.7
C. A chloroform eluate	25.2
D. An ethyl alcohol eluate	5.9
E. An alcoholic potassium hydroxide eluate (acidified and ether-extracted)	5.8
Lost on column	33.7
	<hr/> 100.0

The infrared spectra of all five fractions were traced. Fractions A and E did not show absorption bands at 840 or 890 cm^{-1} . The absorption bands in these fractions appeared in the spectrum of the original acetone extract of the rubber.

The spectra of the remaining three fractions (which increased in hardness in the order B, C, D) all showed absorption bands at 840 and 890 cm^{-1} , and presumably were materials formed from rubber by milling. Absorption bands at 3500 cm^{-1} in all three spectra were due to hydroxyl groups. Fraction C showed carbonyl absorption at 1715 cm^{-1} , presumably aldehydic or ketonic. Fractions B and D showed a carbonyl absorption band between 1730 and 1740 cm^{-1} . This is a high frequency for an aldehyde or ketone and it is unlikely an ester would be formed. From spectral considerations the band might be due to an acid, but benzene and ethyl alcohol do not eluate acids from aluminum oxide columns⁶. The origin of this band is, therefore, unknown.

TABLE 1
AMOUNTS OF FRACTIONS OF EXTRACTS AFTER MILLING

	Approx. temp. rolls ($^{\circ}\text{C}$)	Not milled					
		670	475	390	335	254	135
	Plasticity (1/100 mm.)	0.036	0.107	0.099	0.108	0.201	0.221
	Total extract after milling (%)	0.004	0.013	0.008	0.009	0.016	0.008
A.	Benzene insoluble (%)	0.011	0.019	0.037	0.036	0.042	0.047
B.	Benzene eluate (%)	0.002	0.015	0.017	0.021	0.036	0.045
C.	Chloroform eluate (%)	0.001	0.004	0.006	0.008	0.009	0.018
D.	Alcohol eluate (%)	0.009	0.015	0.013	0.009	0.015	0.014
E.	Potash eluate (%)						

The absorption bands in the infrared spectra of fractions C and D appear in the spectrum of fraction B, but, whereas the spectra of C and D do not indicate contamination, the spectrum of fraction B does suggest absorption due to other components in the region 950 to 1200 cm^{-1} . The infrared spectrum of the normal acetone extract of the rubber used does show many absorption bands in this region. A benzene eluate was obtained when unmilled rubber was extracted for a second time, and this extract was fractionated chromatographically. Accordingly the contamination of fraction B was due to the presence of part of the original acetone extract of the rubber (see also Table 1).

The conclusion drawn from the infrared spectra that only fractions B (mainly), C, and D consist of materials formed from rubber by milling is confirmed by the results in Table 1. These show that the amounts of these fractions increase with increasing mastication, independently of roll temperature, while the amounts of fractions A and E remain more or less constant.

The infrared spectrum of the acetone distilled from the second extract was identical with the spectrum of acetone. Therefore if any volatile substances were broken from the rubber during milling, they were lost to atmosphere during the mastication process.

ACETONE EXTRACT OF AGED RUBBER

In a further experiment, acetone-extracted rubber was aged in an air oven for forty hours at 70° C, and then extracted again with acetone. The second extract (amounting to 0.064 per cent of the rubber) was fractionated as previously described. The five fractions were obtained in approximately the same proportions as when rubber was milled and not aged. The infrared spectra of the five fractions were traced and were similar to the corresponding fractions obtained from milled rubber.

DISCUSSION

The infrared spectra of the fractions of the acetone extracts obtained after masticating and aging pale crepe rubber do not indicate any differences between the acetone-soluble materials produced during the aging and masticating processes. It therefore seems likely that the acetone-soluble substances produced during mastication are a result of an autoxidation sequence of reactions.

During mastication normal autoxidation of rubber occurs, but since 0.139 per cent of acetone extract was obtained after fifteen minutes' milling (approximately 0.10 per cent of which was produced by the milling, the remainder being residual normal acetone extract) and only 0.064 per cent of extract was obtained after forty hours' heat aging (approximately 0.03 per cent formed by aging), the contribution of normal autoxidation to the acetone-soluble materials produced during the relatively short milling process would appear negligible.

The currently accepted mechanism of mastication in air, advanced by Pike and Watson⁶, is:

- (1) $R - R \rightarrow R \cdot + R \cdot$ mechanical rupture.
- (2) $R \cdot + O_2 \rightarrow RO_2 \cdot$ oxygen intervention preventing recombination.
- (3) $RO_2 \cdot \rightarrow$ stable molecule.

From the results reported in this paper, it is suggested that one course for Reaction 3 is for the oxygenated radical to abstract an α -methylene hydrogen atom inter- or intramolecularly. This transforms the radical to a molecule and at the same time initiates an autoxidation chain reaction. The acetone-soluble materials produced during mastication are, therefore, according to this hypothesis, the result of a secondary reaction, the main chain scission not directly producing acetone-soluble molecules. It is to be expected that acetone-soluble materials would be formed if mechanical scission occurred near the end of a chain (the molecule which would form would have a relatively short hydrocarbon chain, with an oxygen group at one end). It would appear from the extract results that scission does not occur near rubber chain ends, for this would produce different acetone-soluble substances from normal autoxidation. Perhaps the anchorage of a short length of rubber molecule in the rubber mass is not sufficient to hold against the applied mechanical forces, and the length does not break off, but is pulled free.

CRYSTALLIZATION AND STORAGE

Masticated rubber crystallizes more readily than unmasticated rubber on cooling, and the greater the extent of mastication the harder the rubber eventually becomes⁷. The acetone-soluble substances produced during mastication contain both hydroxyl and carbonyl groups. It is expected that such groups are also present in the non-acetone soluble degradation products. Hydrogen bonds can form between hydroxyl and carbonyl groups⁸ and may, therefore, be present in masticated rubber. The longer rubber is masticated, the more hydroxyl and carbonyl groups are produced, a greater number of hydrogen bonds can form and the harder the rubber becomes on freezing. It is significant that removal of hydrogen bonding capacity in polyamides reduces crystallinity and the polymers become rubberlike⁹. The molecular weight of masticated rubber, measured in dilute solution, was the same before and after freezing¹⁰, but hydrogen bonds would be unstable under such conditions⁸.

It is known that masticated rubber toughens during storage at normal temperatures, and Watson has suggested¹¹ that possibly a free radical mechanism is responsible. It is now suggested this toughening is a hydrogen bonding effect. This is a mechanism considered worthy of further investigation.

SUMMARY

Acetone-soluble substances formed during the milling of rubber were divided by chromatographic analysis into three fractions. Infrared spectra of these fractions were identical with the spectra of corresponding fractions from heat-aged raw rubber. The significance of these results is discussed in conjunction with Pike and Watson's subsequent theory of cold mastication mechanism.

ACKNOWLEDGMENTS

The work described is one aspect of investigations on mastication mechanism which were made at the National College of Rubber Technology during 1948 to 1951.

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REFERENCES

- ¹ For a review, see Lee, *Rubber India* 5, No. 4, 21; No. 5, 24 (1953).
- ² Weber, *India-Rubber J.* 25, 639 (1903); Shacklock, *Trans. Inst. Rubber Ind.* 7, 354 (1932).
- ³ For tables relating absorption bands to characteristic groups, see Mann, *J. Rubber Research Inst. Malaya* 18, 79 (1949).
- ⁴ Dinmore and Smith, *Anal. Chem.* 20, 11 (1948).
- ⁵ Bellamy, Lawrie, and Press, *Trans. Inst. Rubber Ind.* 22, 312 (1947).
- ⁶ Pike and Watson, *J. Polymer Sci.* 9, 229 (1952); Watson, *Trans. Inst. Rubber Ind.* 29, 32 (1953).
- ⁷ Katz, *Gummi-Ztg.* 41, 2036 (1927); Gehman, *Chem. Rev.* 26, 293 (1940); Cotton, *Trans. Inst. Rubber Ind.* 16, 303 (1941); Ph.D. Thesis, London Univ. 1948, p. 35.
- ⁸ Hunter, *J. Chem. Soc.* 1945, p. 806; *Ann. Rept. Chem. Soc.* 43, 151 (1946).
- ⁹ Lewis and Reynolds, Symposium Polymer Chem. London, 1950, Preprint No. 8.
- ¹⁰ Cotton and Lee, *India-Rubber J.* 120, 919 (1951).
- ¹¹ Watson, *Trans. Inst. Rubber Ind.* 29, 40 (1953).

ELECTRON MICROSCOPIC STUDIES OF FILLERS IN RUBBER. III. EFFECT OF MILLING ON THE DISPERSION OF FILLERS *

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INTRODUCTION

In the study of types of fillers which have a marked effect on the properties of rubber, information as to how the filler particles are dispersed in rubber is a prerequisite. The authors have already reported¹ on the state of dispersion of various fillers in vulcanized rubber, observed under an electron microscope by the replica method. How the dispersion of these fillers affects the properties of rubber is an interesting problem. Since, in the earlier work, filler particles were observed to orient themselves in certain directions, in this report the relationship between the state of dispersion observed under an electron microscope of filler particles in rubber milled in different ways and the resulting characteristics of the mixtures were examined.

EXPERIMENTAL

RUBBER SAMPLES

A masterbatch was prepared from raw rubber by mixing with an accelerator, zinc oxide, stearic acid, and sulfur. This was divided into four equal parts, and two kinds of calcium carbonate (Hakuenka-CC and weakly acidic calcium car-

TABLE 1

Weight ratio	Mixture I	Mixture II
Smoked sheet	100	100
Zinc oxide	5	5
Stearic acid	1	1
Sulfur	3	3
Accelerator M	1	1
Hakuenka-CC	100	—
Weakly acidic calcium carbonate	—	100

bonate) were added by ordinary milling and by simplified milling in accordance with the recipes given in Table 1. The ordinary milling operation involved thorough mastication of the rubber by the usual reversal method and taking off a thin sheet. The simplified method of milling was to mix in a filler without

* Translated from RUBBER CHEMISTRY AND TECHNOLOGY from the *Journal of the Society of the Rubber Industry of Japan*, Vol. 28, No. 9, pages 1-5 (1955).

reversing the mix taken off and then removing as a thin sheet. The conditions of milling were as follows:

Mill rolls.—8 × 16 inches, rotating at 14 r.p.m., and with friction ratio of 1:14.

Milling of masterbatch.—To 1200 grams of previously roughly milled raw rubber were added the accelerator M, stearic acid, zinc oxide, and sulfur in this order. In this way 1320 grams was mixed in 17 minutes.

Mixing of fillers.—To the masterbatch mentioned above, divided into four equal parts of 330 grams each, was added each of the two calcium carbonate samples and then milled by the ordinary method and by the simplified method so as to obtain the following four mixtures:

Mixture	Milling	Time of milling (min.)
I-1	Ordinary	11
I-2	Simplified	9
II-1	Ordinary	9
II-2	Simplified	6

Surface temperature of mill rolls about 50°; distance between the rolls 0.7 mm.; distance between the rubber guides 12 cm.; amount milled 630 grams.

Vulcanization.—Press-vulcanized at 40 lbs./sq. in. for 20 minutes. One hundred grams of rubber was cured in a metal mold 17 × 21 cm. and 0.2 cm. deep.

From these vulcanizates dumbbell-shaped test-pieces were cut out in longitudinal and transverse to the direction of milling. These were then tested for tensile strength. The results are given in Table 2.

TABLE 2

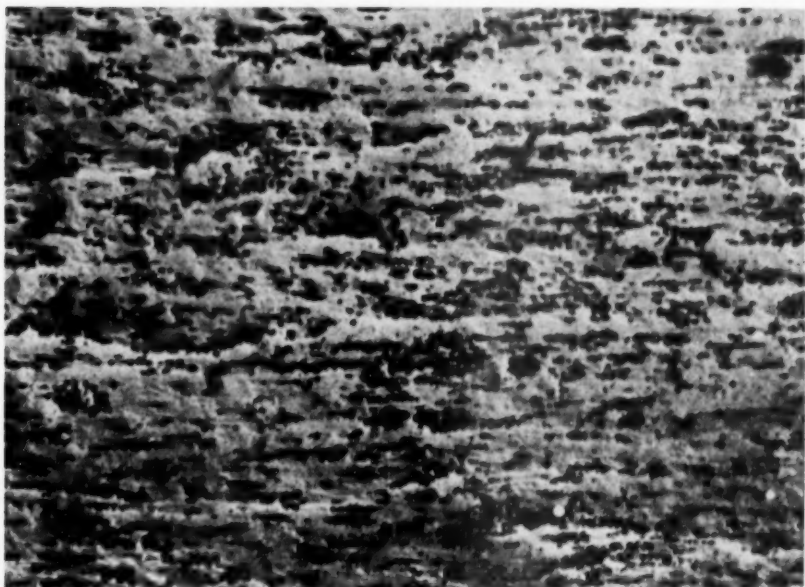
Mixture	Milling method	Direction of sheet	Modulus (kg./sq. cm.)		Tensile strength (kg./sq. cm.)	Elongation (%)
			300%	500%		
I-1	Ordinary	Longitudinal	39.6	100	210	680
		Transverse	35.6	96.2	200	690
I-2	Simplified	Longitudinal	38.6	105	205	675
		Transverse	35.2	94.9	193	685
II-1	Ordinary	Longitudinal	47.9	117	157	585
		Transverse	46.0	112	151	580
II-2	Simplified	Longitudinal	46.2	114	154	585
		Transverse	45.9	110	147	585

OBSERVATIONS UNDER AN ELECTRON MICROSCOPE

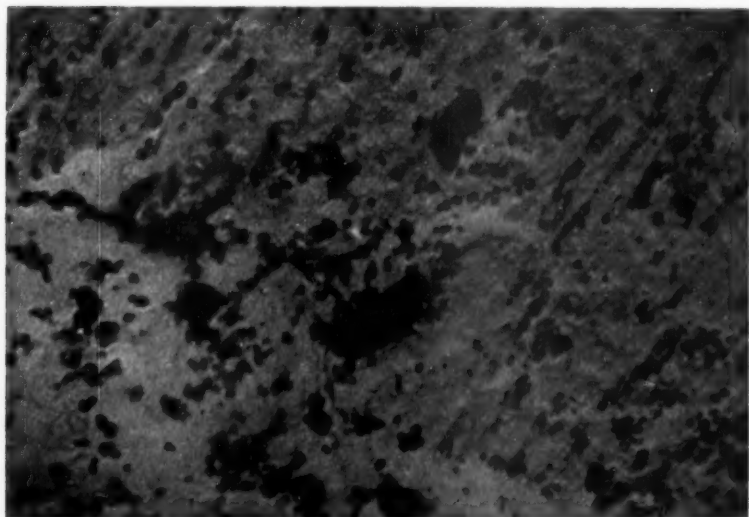
The electron photomicrographs of the eight samples shown in Table 2 were made by the replica method. The procedure has already been described², and is omitted here. However, in the earlier work, the methylmethacryl-aluminum two-step replica method was used, but in the present work the methylmethacryl-silica two-step replica method was used in its place. Silica gave a more beautiful and stronger replica membrane surface than did aluminum. For the negatives, chromium was used, as in the previous work.

RESULTS

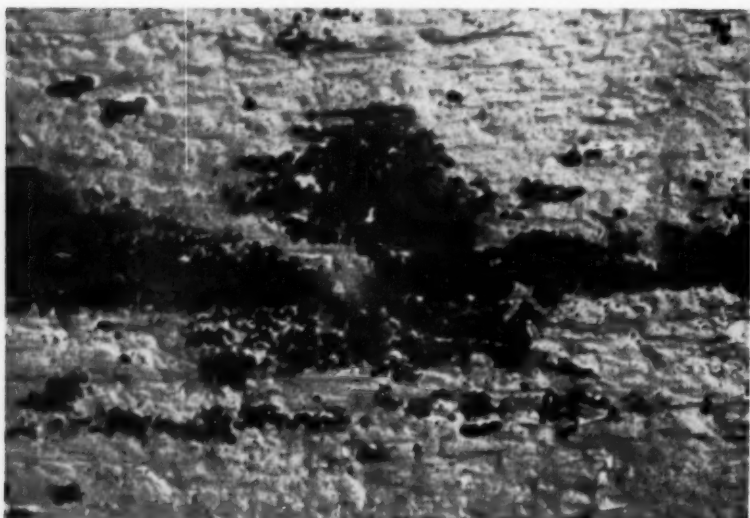
The typical electron photomicrographs of the samples thus obtained are given in Photomicrographs nos. 1 to 8.



PHOTOMICROGRAPH 1.—Cross-section of rubber mixed with Hakuenka CC and milled by the ordinary method. Longitudinal to the direction of milling. $\times 15,000$.



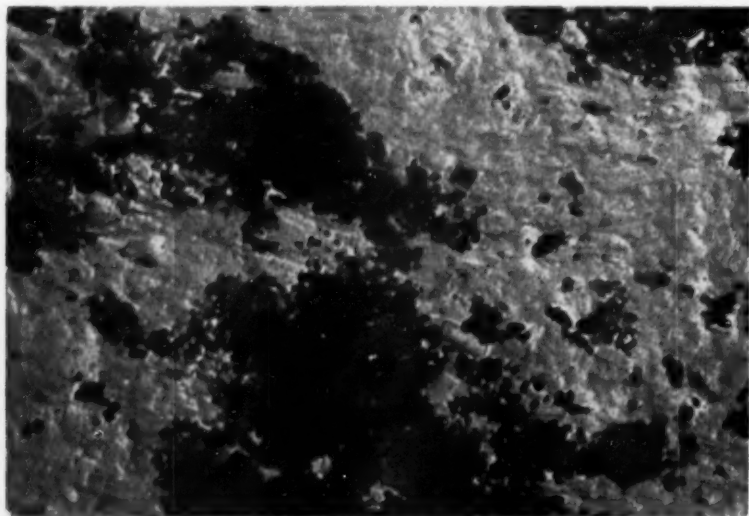
PHOTOMICROGRAPH 2.—Cross-section of rubber mixed with Hakuenka CC and milled by the ordinary method. Transverse to the direction of milling. $\times 15,000$.



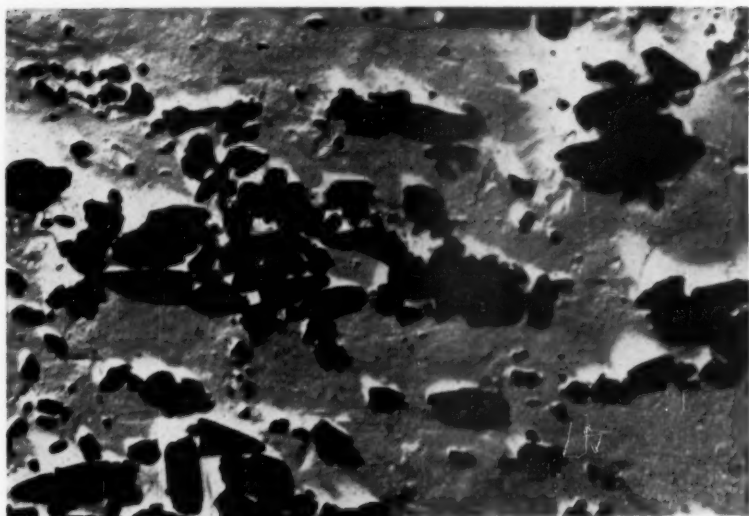
PHOTOMICROGRAPH 3.—Cross-section of rubber mixed with Hakuenka CC and milled by the simplified method. Longitudinal to the direction of milling. $\times 15,000$.

SAMPLE LOADED WITH HAKUENKA-CC

As mentioned earlier², the Hakuenka-CC was composed of fairly uniform rhombohexahedral particles about $40\text{ m}\mu$ in size. Typical electron photomicrographs of the sample containing this filler and milled by the ordinary method



PHOTOMICROGRAPH 4.—Cross-section of rubber mixed with Hakuenka CC and milled by the simplified method. Transverse to the direction of milling. $\times 15,000$.

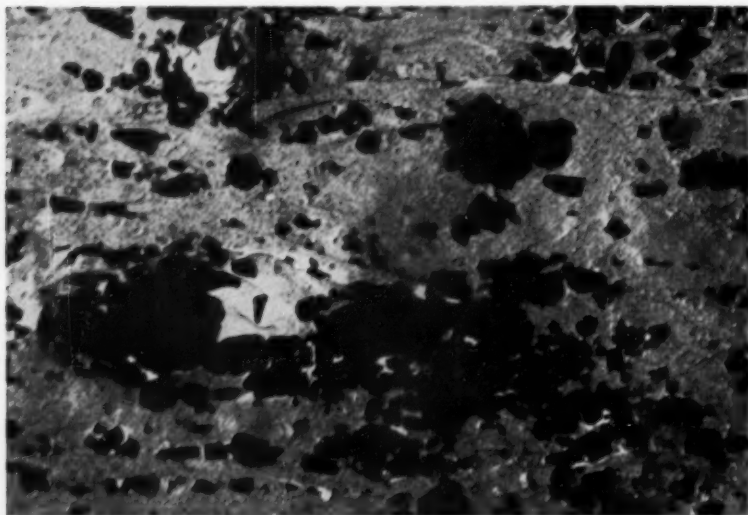


PHOTOMICROGRAPH 5.—Cross-section of rubber mixed with weakly acidic calcium carbonate by the ordinary method. Longitudinal to the direction of milling. $\times 9000$.

and by the simplified method are shown in Photomicrographs 1-4 for cross-sections longitudinal and transverse to the direction of milling. Photomicrograph 1 shows the cross-section in the direction of milling of a sample milled by the ordinary method. The filler particles are seen beautifully arranged in parallel rows. Photomicrograph 2 shows the cross-section transverse to the direction

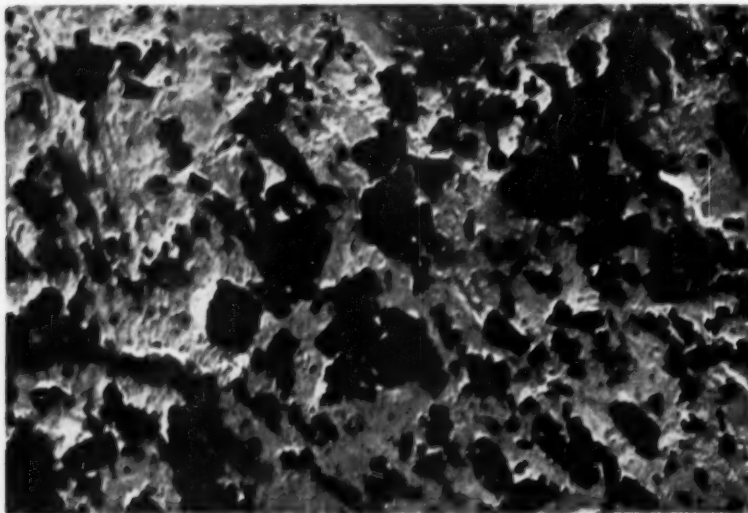


PHOTOMICROGRAPH 6.—Cross-section of rubber mixed with weakly acidic calcium carbonate by the ordinary method. Transverse to the direction of milling. $\times 9000$.



PHOTOMICROGRAPH 7.—Cross-section of rubber mixed with weakly acidic calcium carbonate and milled by the simplified method. Longitudinal to the direction of milling. $\times 9000$.

of milling, which can be clearly distinguished from the longitudinal cross-section by the vortexes of particles as a whole, although parallel rows are seen in some parts. This tendency is also evident in the sample milled by the simplified method. Here the dispersion of filler particles is naturally poorer because the mix was not reversed or sheeted out thin. Photomicrograph 3 shows a cross-



PHOTOMICROGRAPH 8.—Cross-section of rubber mixed with weakly acidic calcium carbonate and milled by the simplified method. Transverse to the direction of milling. $\times 9000$.

section longitudinal to the direction of milling of a sample milled by the simplified method. The particles are clumped, not dispersed, yet clearly extended in one direction as apparent chains of clumps. On the other hand, the cross-section transverse to the direction of milling of the sample prepared by the simplified method, as seen in Photomicrograph 4, shows no such orientation of particles.

SAMPLE LOADED WITH WEAKLY ACIDIC CALCIUM CARBONATE

As mentioned in previous works³, the weakly acidic calcium carbonate was composed of spindle-shaped particles, with the ratio of the long axis to the short axis about 4:1. The state of filler particles in the sample milled by the ordinary method and cross-sectioned in the direction of milling is shown in Photomicrograph 5. Here the tendency of filler particles to arrange themselves generally in one direction is seen. That is, the long axes of the spindles tend to lie in the

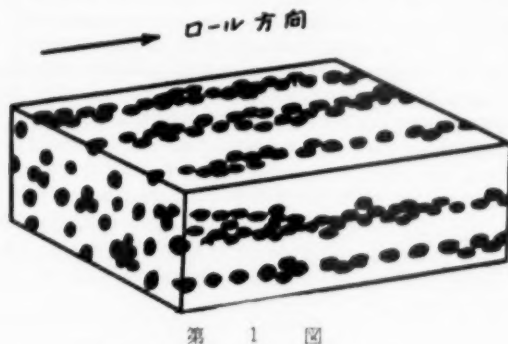


Fig. 1.—Arrow indicates direction of milling.

direction of milling. The cross-section transverse to the direction of milling of this sample, as seen in Photomicrograph 6, shows complete mixing of particles, with no orientation whatsoever. In the case of simplified milling, as seen in Photomicrographs 7 and 8, no clear orientation is evident in either cross-section.

DISCUSSION

The differences in physical properties of rubber according to the direction of milling has already been reported⁴. In general, the tensile strength and modulus are lower in rubber in the direction transverse to the direction of milling. The differences depend on the kind and quantity of fillers used, the method of milling, and the vulcanizing conditions. As shown in Table 2, the samples used in this experiment show such a tendency. This phenomenon is related, according to current theories, to the grain or calender effect of rubber, which in turn depends on the molecular orientation of rubber and the arrangement of filler particles. The effect of the former disappears largely with vulcanization and other heat treatments, and therefore can not be observed under an electron microscope. The effect of the latter is evident in the results of this experiment.

The arrangement of filler particles, as observed under an electron microscope, is shown diagrammatically in Figure 1. In the longitudinal cross-section,

the filler particles are clearly seen to be arranged along the direction of milling, but in the cross-section transverse to the direction of milling, no such orientation of particles is evident. In Figure 1 the filler particles in the transverse cross-section are irregularly arranged, as they ordinarily are. Moreover, the number of particles per unit area, that is, the particle density, is the same in any transverse cross-section. On the contrary, the particle density in the longitudinal cross-section shows spottily very high and low parts.

In the elongation test, the rubber samples stretched more easily in the transverse direction than in the longitudinal direction because of the presence of lower density zones of filler particles, and showed in general lower tensile strengths because of the presence of higher density zones of filler particles. With a small amount of filler in the rubber, the difference between the high and low particle densities becomes small, thus diminishing the effect of particle arrangement.

Compared to the ordinary milling process discussed above, the simplified method of milling, especially with such minute particles, such as Hakukenka-CC, the aggregation of filler particles became naturally very marked. Even then, the orientation of particles in the cross-section in the direction of milling is evident. Because of such poor dispersion of filler particles, the physical properties of rubber milled by the simplified method are inferior to those of rubber milled by the ordinary method. With smaller filler particles, more prolonged milling is naturally required.

ACKNOWLEDGMENTS

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REFERENCES

- ¹ Suito, Arakawa, Hasegawa, and Furusawa, *J. Soc. Rubber Ind. Japan* 26, 453 (1953).
- ² Suito, Arakawa, and Hasegawa, *J. Soc. Rubber Ind. Japan* 26, 216 (1953).
- ³ Suito, Arakawa, Hasegawa, and Furusawa, *J. Soc. Rubber Ind. Japan* 26, 453 (1953); Suito, Arakawa, and Hasegawa, *J. Soc. Rubber Ind. Japan* 26, 216 (1953).
- ⁴ Vogt and Evans, *Ind. Eng. Chem.* 15, 1015 (1923); Wiegand and Braendle, *Ind. Eng. Chem.* 15, 259 (1923); Ishokuro, *J. Soc. Rubber Ind. Japan* 10, 239 (1937); Koide, Kubota, and Shimoda, *J. Soc. Rubber Ind. Japan* 24, 227 (1951).

THE PROTEINS OF HEVEA BRASILIENSIS LATEX.* I. PROTEIN COMPONENTS OF FRESH LATEX SERUM

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Analytical studies¹ have shown that fresh unammoniated Hevea latex contains about 1 per cent of protein, part of which is adsorbed at the surface of the rubber particles, while the remainder is distributed between the aqueous serum phase of the latex and the luteoid substances first described by Homans and van Gils². Although it is generally recognized that the presence of protein in fresh latex is an important factor controlling its colloidal stability, further information on the concentration and properties of the individual protein components, and their distribution between the above three phases, is necessary for a better understanding of the colloidal behavior of latex.

The present paper describes investigations on the proteins of fresh latex serum. Before 1942 the presence of three protein fractions in fresh serum had been demonstrated³. Similar fractions were also obtained from ammonia-preserved latex, though the presence of ammonia modified the properties of the proteins in some respects⁴. Later, a more detailed electrophoretic analysis of the proteins in unammoniated serum was carried out by Roe and Ewart⁵, who demonstrated the presence of seven electrophoretically distinct protein components.

The present paper confirms and extends many of Roe and Ewart's results. It is shown that the properties and composition of latex serum prepared by prolonged freezing of fresh latex differ in certain important respects from the serum obtained by centrifuging the latex.

EXPERIMENTAL

MATERIALS

Freeze-dried serum.—All experiments were carried out with latex from the same eighteen mixed clonal seedlings growing at the Rubber Research Institute of Malaya Experiment Station, and tapped regularly by a half-spiral, alternate-day tapping system. Latex collected in glass vessels surrounded by a mixture of ice and salt did not separate into three distinct fractions on high-speed centrifuging (see below) and did not yield a clear serum after coagulation by deep freezing. The latex was, therefore, collected at normal temperature in clean aluminum tapping cups. The collection period was limited to 30 minutes, and the first runnings from the tree were not included in the samples.

* Reprinted from the *Biochemical Journal*, Vol. 61, No. 3, pages 593-597 (1955).

Serum was obtained from the latex in two ways. The first consisted of freezing the latex at -25° for a period of 15 days or more⁶. The frozen mass was broken up into small pieces to expose a large surface to the air; after thawing, the rubber separated completely, leaving a clear serum which could be decanted and freeze-dried. The serum so obtained is described here as *F* serum. The method of preparation is essentially the same as that used by Bishop⁷ and by Roe and Ewart⁸. If appreciably less than 15 days' freezing at -25° was allowed, or the frozen latex was not broken up, coagulation was often incomplete and a milky serum resulted.

Alternatively, the freshly tapped latex was treated as rapidly as possible, by centrifuging at 59,000 g in an ultracentrifuge at 5° . After 45 minutes at speed, the serum had separated as an almost clear middle layer, with a heavy fraction at the bottom and a rubber layer at the top of the centrifuge tube⁹. The serum could be run off by making two small punctures in the celluloid centrifuge tube, one near the bottom of the serum layer, the other near the top. This material, described in the present paper as *C* serum, was stored at -25° until a second collection and centrifuging had been made two days later. The sera from the two collections were bulked and freeze-dried together.

When dry, the serum solids were transferred to smaller glass tubes; the moisture absorbed during transfer was removed under vacuum and the tubes sealed off. Samples were stored in this condition, preferably at 0° , until ready for use.

METHODS

Elementary analyses.—C, H, and ash determinations were made by Pregl microcombustion, and total N by the micro-Kjeldahl method. P was determined colorimetrically with ammonium molybdate, after wet oxidation. The S content of the ash and gaseous products after microcombustion was determined turbidimetrically as BaSO_4 after complete dissolution of the ash in dilute HCl. All samples were dried to constant weight *in vacuo* at room temperature before analysis.

Protein nitrogen.—Three methods were examined for the determination of protein N, viz., precipitation with saturated ammonium sulfate, with 20% (w/v) trichloroacetic acid or with 0.5% tannic acid:

(a) A 1% solution of the serum solids was saturated with ammonium sulfate and set aside for 24 hours at 0° . The precipitate was centrifuged off and freed from sulfate by dialysis in cellophane at 0° . The resulting suspension was then freeze-dried, brought to constant weight at 105° , and analyzed for N.

(b) A 40% (w/v) solution of trichloroacetic acid was added to an equal volume of the serum-solids solution (1%, w/v) and the precipitate centrifuged down. In this case, protein N could be determined conveniently by the difference in N content of the clear supernatant and the original solution. Alternatively, the precipitate was washed by resuspending in dilute trichloroacetic acid and recentrifuging; the product was then dried as in (a) and analyzed.

(c) The same procedure was followed as in (b), but a 1% solution of tannic acid was used instead of trichloroacetic acid. Protein N was normally determined by difference. Corrections were made, when necessary, for the N content of the tannic acid (or trichloroacetic acid in (b)).

The *C* solids were usually contaminated by small amounts of rubber present in the original latex as very small particles, which were not separated completely at the highest centrifuge speeds attained. On analysis of the precipitated pro-

tein directly for N, it was therefore necessary to extract the precipitate with benzene before drying it at 105°.

Paper electrophoresis.—For determining the number of electrophoretically distinct proteins in the serum solids, paper electrophoresis on Whatman no. 1 paper was used. The apparatus was a modification of that described by Kunkel and Tiselius⁹, with 0.05M sodium veronal buffer (pH 8.6) as the solvent medium. To improve resolution of the proteins, the paper was separated from the supporting plates by narrow strips of polythene 0.06 inch thick, parallel to the edges of the paper. After electrophoresis had proceeded under a potential gradient of 4.5 v/cm. for 1000 minutes, the paper was dyed with 1% bromophenol blue in ethanol, as recommended by Kunkel and Tiselius. Electroendosmotic flow was corrected for by the use of dextran.

After drying, the paper was cut into strips and the amount of dye on each strip determined absorptiometrically after elution with 0.01M NaOH. Later, an EEL photoelectric scanner¹⁰, which gave much more rapid results than the dye-elution technique, was used.

TABLE I
ELEMENTARY ANALYSIS OF DRY SERUM SOLIDS

	%						Protein N*	Non-protein N*	Protein content (see text)*
	C	H	N	S	P	Ash			
Average for 27 <i>F</i> samples	37.6	6.19	4.01	0.23	1.04	13.5	1.93	2.08	12.8
Standard deviation	0.66	0.10	0.37	0.07	0.25	1.10	—	—	—
Average for 6 <i>C</i> samples	39.7	6.43	4.52	0.16	0.74	11.4	2.7	1.82	17.8
Standard deviation	0.38	0.15	0.20	0.02	0.14	1.20	—	—	—

* Determined on samples of average total N content.

The determination of protein concentration along the paper has not been attempted, in view of the arbitrary assumptions involved in such determinations¹¹.

RESULTS

Analyses of latex-serum solids.—An extensive analysis of thirty-three samples, collected over a period of 18 months, is summarized in Table 1.

With the *F* solids, the three methods of determining protein N, referred to above, gave concordant results. Completeness of precipitation was shown by dialyzing the filtrates against water at 0° for 72 hours, after which a negative biuret test was obtained. The N content of the dried precipitate was 15.2 (±0.2) per cent. For converting protein N into percentage protein, a conversion factor of 6.58 is therefore recommended for the total proteins.

With solutions of the *C* solids, precipitation of protein by saturated ammonium sulfate was incomplete, the filtrate yielding a further precipitate on heating to 100°. Precipitation with 20 per cent trichloroacetic or 0.5 per cent tannic acid yielded filtrates which gave no further precipitate on heating, and methods (b) and (c) were therefore used for the protein N determinations. The N contents of the dried products were in good agreement with those found for the precipitated proteins from *F* solids. The same conversion factor of 6.58 can, therefore, be used to convert protein N into percentage protein. However, the yield of protein from the *C* solids was relatively high (17.8 per cent),

corresponding to a protein N content of 2.7 per cent. Determination of the protein N by difference, from analysis of the supernatant, gave the same result (Table I).

pH changes in reconstituted serum.—The *F* solids dissolved readily in distilled water to give clear pale-yellow solutions. *C* solids also dissolved readily, giving almost colorless solutions which were slightly hazy. In both cases the solutions, when freshly prepared, possessed a slight but pleasant odor.

At concentrations of 5 and 0.5 per cent (w/v) the *F* solutions had pH values of 6.4 ± 0.1 and 6.6 ± 0.1 respectively immediately after dissolution. No change in pH occurred on allowing these solutions to stand in air at 20° for several hours. The pH values of the *C* samples immediately after dissolving were considerably higher and varied between pH 7.3 and 8.1, at 5 per cent concentration. On standing in air at 20°, the pH of these solutions decreased rapidly (Figure 1), all reaching pH 6.6 ± 0.15 after 3 hours (curve *b*). An

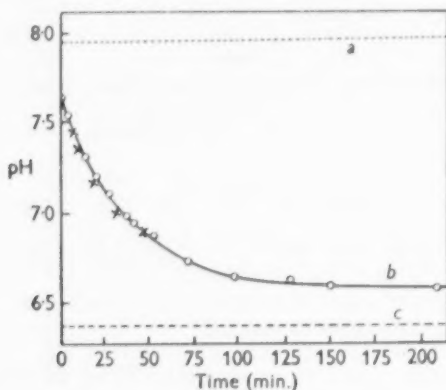


Fig. 1.—pH changes in 5 per cent (w/v) solutions of Hevea latex-serum solids in distilled water: (a) *C* serum heated to 90° and cooled; (b) *C* serum in air (O) or N_2 (X); (c) *F* serum.

identical rate of fall of pH occurred when the solutions were kept under pure nitrogen. When a freshly prepared solution of the *C* solids was heated at 90° for 5 minutes (curve *a*), no subsequent fall of pH occurred after cooling (the heat treatment itself usually produced a small increase in pH of about 0.3 unit). The fall of pH in solutions of the *C* solids is probably due in part to production of hydrogen sulfide, which could be detected by lead acetate paper after the solutions had been set aside for half an hour or more in a closed vessel.

Protein components of reconstituted serum.—The number of individual proteins (or proteoses) in the *F* solids, detectable by electrophoresis, was determined by first precipitating the total protein with saturated ammonium sulfate. Excess of sulfate was removed by dialysis at 0° against 0.05*M* veronal buffer (pH 8.6). A solution of the total protein in the buffer was then subjected to electrophoresis on paper. A typical electrophoretic diagram is shown in Figure 2, in which the individual protein fractions have been numbered 1–7 in order of increasing anionic mobility. It is clear that fraction 1 is positively charged at pH 8.6. Figure 2 shows many resemblances to the schlieren diagrams at pH 8.43 obtained by Roe and Ewart⁶ for the frozen latex serum of Florida and

Sumatra latex. The lettering of the individual protein fractions given by these authors appears to be related to ours in the following way (our protein no. 2 was not detected by Roe and Ewart; protein VII described by them has not been detected by us):

Roe and Ewart	I	II	III	IV	V	VI	VII	—
Present work	4	6	1	3	5	7	—	2

Since precipitation by trichloroacetic acid or tannic acid results in the irreversible coagulation of some of the protein components, and precipitation by saturated ammonium sulfate is incomplete with the *C* solids, solutions of the latter were prepared for electrophoresis by dialyzing, at 0°, a concentrated solution of the solids against 0.05*M* veronal buffer (pH 8.6) for 24 hours. A typical electrophoretic diagram is included in Figure 2. Protein no. 7 has not been detected in all samples tested.

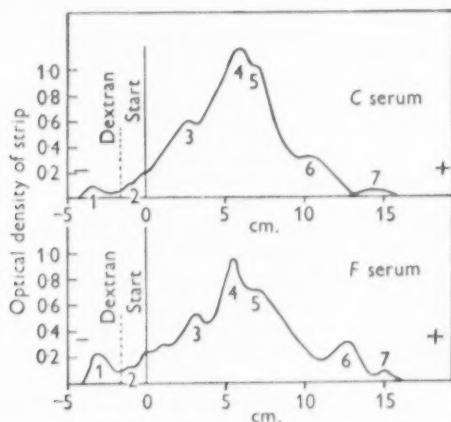


FIG. 2.—Paper electrophoresis of Hevea latex-serum proteins. Electrophoresis for 1000 minutes in 0.05*M* sodium veronal buffer (pH 8.6) at 4.5 v/cm. The ordinates represent the optical density of the strip in arbitrary units.

Effect of ammonia on the proteins of F serum.—Roe and Ewart⁵ found that when the serum from frozen latex was treated with ammonia, the number of protein components detectable by electrophoresis decreased until, after several months, only two components of the original seven could be detected. Although it is not entirely clear which these two components were, the one present in the larger concentration appeared to be either protein 4 or 5, in our nomenclature. It was noticed that the ammonia also produced a gradual increase in the anionic mobility of this constituent.

In the present work, samples of the same sample of *F* solids were stored in 1.2 per cent (w/v) aqueous NH_3 at 18° for different times. The solutions were then neutralized with dilute H_2SO_4 and the total protein was precipitated by saturation with ammonium sulfate. After centrifuging, the precipitates were mixed to pastes with water and dialyzed against 0.05*M* veronal buffer, and the resulting solutions analyzed by paper electrophoresis. The results (Figure 3) show:

(a) The concentration of one of the main protein components (no. 4) of the original solution decreases rapidly and is barely discernible after 15 days' ammoniation. The concentration of the other main component (no. 5) appears to be largely unaffected by the ammonia.

(b) Components 2 and 3 are no longer detectable after 15 days' ammoniation.

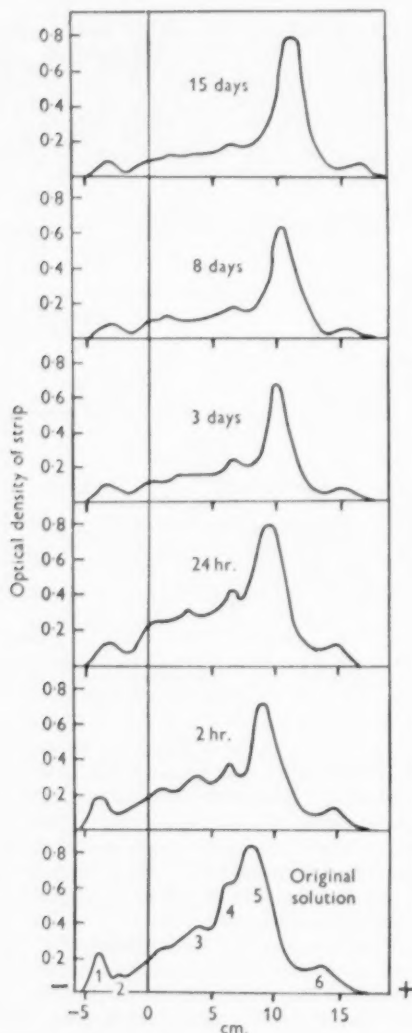


FIG. 3.—Effect of ammonia (1.2 per cent w/v) on the electrophoresis diagram of *F* serum. Initial position of the proteins is indicated by the vertical line. The times refer to the period of contact with ammonia before electrophoresis. Electrophoresis carried out in 0.05*M* sodium veronal buffer (pH 8.6) for 1000 minutes at 4.5 v/cm.

(c) The concentrations of components 1 and 6 diminish slowly.

(d) The anionic mobilities of components 5 and 6 increase, and the cationic mobility of component 1 decreases slightly, as the time of contact with ammonia increases. The mobility of component 4 does not change appreciably with time.

DISCUSSION

It is apparent from Table 1 that the percentage of oxygen in fresh latex-serum solids must be high (about 40 per cent), as would be expected from the fact that the polyhydric alcohol quebrachitol is known to be a major component of the serum¹². At least part of the difference between the carbon and hydrogen contents of the *F* and *C* material was due to the *C* material still containing small amounts of rubber hydrocarbon. The ratio of protein nitrogen to total nitrogen is approximately 50 per cent in the *F* and 60 per cent in the *C* solids. The difference in the actual protein contents indicates that nearly 30 per cent of the serum protein in fresh latex is lost by coagulation during long freezing of the latex. The possibility of some hydrolysis of protein during this process cannot be ruled out, in view of the slightly higher nonprotein nitrogen content of the *F* solids. However, the fact that the phosphorus content is also appreciably higher in the *F* material suggests that it is phospholipid, initially associated with the rubber particles, which is partially hydrolyzed during the freezing process with passage of phosphorus and base nitrogen into the serum phase. The ready hydrolysis of latex phospholipids has been demonstrated by previous workers¹³.

The decrease of the pH value of solutions of the *C* solids in distilled water is attributed to the presence of an acid-producing enzyme or bacteria. With the *F* material, this enzymic or bacterial action has already proceeded sufficiently far, apparently, to give a constant pH of approximately 6.5. Roe and Ewart⁸ also observed that the pH of unammoniated serum prepared from frozen latex was 6.4 and that the serum could be kept at -20° for several months without change.

The electrophoretic diagrams for the *F* and *C* solids (Figure 2) are very similar, indicating that the difference between the solids is mainly one of protein concentration. However, a difference in the nature of one or more proteins is indicated by the incomplete precipitation of protein from the *C* solids by saturation with ammonium sulfate and the appearance of a further precipitate on heating to 100° . From Figure 2, proteins nos. 4 and 5 appear to be the main components in both *F* and *C* solids.

Our results showing the effect of ammonia on the proteins of *F* serum are consistent with those of Roe and Ewart⁸, if allowance is made for the different storage periods. The two proteins observed by these authors after prolonged ammoniation were presumably components 1 and 5. The predominating importance, as regards concentration, of protein no. 5 in the ammoniated serum, is apparent.

SUMMARY

1. The aqueous serum phase of unpreserved rubber latex (*Hevea brasiliensis*) has been separated in two ways: (a) by high-speed centrifuging, and (b) by prolonged freezing at -25° . The protein contents of the serum solids are approximately 18 and 13 per cent, respectively; the difference is attributed to coagulation of protein during prolonged freezing of the latex.

2. There is evidence that organic phosphorus compounds (probably phospholipids) are partially hydrolyzed during the freezing process, and that enzymic or bacterial reactions occur, leading to a fall of pH of the serum.

3. In both types of serum, seven-electrophoretically distinct protein components have been detected, one of which is positively charged at pH 8.6.

4. After treatment with dilute ammonia solution for 15 days, only two of the original protein components are readily resolvable electrophoretically. One of these (no. 5) is a major component of the unammoniated serum.

ACKNOWLEDGMENTS

This work forms part of a program of research undertaken by the Boards of the Rubber Research Institute of Malaya and the British Rubber Producers' Research Association. The authors wish to thank E. G. Cockbain for his interest in this work and for his help in the preparation of this paper. Our thanks are also due to Ho Kam Leng for assistance in some of the experimental work, to G. W. Drake and A. I. McMullen for many useful discussions, and to W. T. Chambers and R. J. Thompson for most of the elementary analyses.

REFERENCES

- ¹ Altman, *Rec. trav. chim.* **65**, 919 (1946).
- ² Homans and van Gils, *Proc. 2nd Rubber Technol. Conf.*, London, 1948, p. 292.
- ³ Bishop, *Malayan Agr. J.* **15**, 27 (1927); Kemp and Straitiff, *J. Phys. Chem.* **44**, 788 (1940).
- ⁴ Bondy and Freundlich, *Rubber Age* (N. Y.) **42**, 377 (1938); Kemp and Straitiff, *J. Phys. Chem.* **44**, 788 (1940).
- ⁵ Roe and Ewart, *J. Am. Chem. Soc.* **64**, 2628 (1942).
- ⁶ Sekhar and McMullen, *J. Rubber Res. Inst. Malaya* **13**, 146 (1951).
- ⁷ Bishop, *Malayan Agr. J.* **15**, 27 (1927).
- ⁸ Cook and Sekhar, *J. Rubber Res. Inst. Malaya* **14**, 163 (1953).
- ⁹ Kunkel and Tiselius, *J. General Physiol.* **35**, 89 (1951).
- ¹⁰ Manufactured by Evans Electro Selenium, Ltd., Harlow, Essex, Engl.
- ¹¹ Crook, Harris, Hassan, and Warren, *Biochem. J.* **56**, 434 (1954).
- ¹² Tunnicliffe, *Trans. Inst. Rubber Ind.* **30**, 97 (1954).

II. ISOLATION OF THE α -GLOBULIN OF FRESH LATEX SERUM*

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In Part I of this series¹, some properties of the aqueous serum obtained by freezing or centrifuging the fresh latex of *Hevea brasiliensis* were reported, and the number of individual protein fractions identifiable by paper electrophoresis was determined. The present investigation is concerned with the isolation and properties of one of the two main components, viz., component 5, which is shown to be the chief globulin component of fresh latex serum. To avoid confusion between the lettering and numbering systems of different workers, it is proposed that protein 5 be referred to as the α -globulin component of latex serum. It appears to correspond to component V in the nomenclature of Roe and Ewart² and was almost certainly the main constituent of 'protein A' described by Bishop³, Kemp and Straitiff⁴, and Bondy and Freundlich⁵.

* Reprinted from *Biochemical Journal*, Vol. 61, No. 3, pages 508-512 (1955).

EXPERIMENTAL

MATERIALS

Freeze-dried serum solids prepared by the Rubber Research Institute of Malaya were used throughout. The aqueous serum phase of fresh unammoniated latex was obtained by prolonged freezing or by centrifuging the latex, the serum being then freeze-dried, in the way already described¹. As before, *F* solids and *C* solids refer to the serum solids obtained from fresh serum prepared by the freezing and centrifuging techniques, respectively.

METHODS

Elementary analyses.—N was determined by the micro-Kjeldahl method, and C, H, and ash by Pregl microcombustion. The S content of the ash and gaseous combustion products was measured turbidimetrically as BaSO₄, after complete dissolution of the ash in dilute HCl. P was determined colorimetrically with ammonium molybdate, after wet oxidation. All samples were dried to constant weight at room temperature *in vacuo*, before analysis.

Electrophoresis.—Paper-electrophoresis measurements were carried out as described in Part I¹. 0.05*M* sodium veronal buffer (pH 8.6) being used. Measurements in the Tiselius apparatus were made at 0° and current 5 ma. Solutions for electrophoresis were prepared in veronal buffer (pH 8.6, ionic strength 0.1), the solutions being dialyzed against a large volume of the buffer for 24 hours at 0° before use.

Fractionation of serum proteins.—Two methods were examined:

(a) Following Kemp and Straitiff⁴, solutions of the *F* and *C* serum solids, in distilled water, were partially precipitated with different concentrations of ammonium sulfate at 0°. After 16 hours, the precipitates were centrifuged down and dialyzed for 24 hours against 0.05*M* veronal buffer (pH 8.6) at 0°. The resulting solutions were analyzed by paper electrophoresis.

(b) Total protein was first precipitated from a solution of *F* solids in water by saturation with ammonium sulfate, and the precipitate dialyzed against 0.01*M* trisodium citrate at 0° until free from sulfate. The resulting protein solution was clarified centrifugally and its N content determined. Portions of the solution were then diluted with sodium citrate buffers so as to cover the pH range 4.0–5.2 at ionic strengths varying from 0.02 to 0.25, or the pH range 2.1–3.6 at ionic strength 1.0 (due allowance was made for the trisodium citrate in the protein solution after dialysis). After centrifuging down the precipitates, the clear supernatants were analyzed for N and their pH values checked by means of a glass electrode. All processing was carried out at 0°. The precipitates were dissolved in 0.1*M* veronal buffer (pH 8.6) and examined for homogeneity by paper electrophoresis.

Isolation of purified α -globulin.—The procedure finally adopted for isolating the α -globulin of the latex-serum solids was based on method (b) above. About 40 grams of *F* solids were dissolved in an equal weight of water to give a practically clear solution. Saturated aqueous ammonium sulfate (A.R., 600 ml.) was then added and the mixture maintained at 0° for 1 hour. The precipitated protein was centrifuged off and washed by resuspending in fresh saturated ammonium sulfate. The recentrifuged protein was stirred to a cream with a little distilled water, and dialyzed in cellophane bags against 0.01*M* trisodium citrate at 0° for 48 hours, with several changes of the latter solution, to remove most of the contaminating ammonium sulfate. The resulting solution was

centrifugally clarified and diluted with 0.01M trisodium citrate to give protein N approximately 1.5 mg./ml. The solution was then mixed with 2 volumes of a mixture of equal volumes of 0.0032M trisodium citrate and 0.054M sodium dihydrogen citrate to give a final pH of 4.5. All solutions were cooled to 0° before use.

The precipitated α -globulin was centrifuged off immediately, stirred to a smooth cream with a little water, and redissolved by the gradual addition of

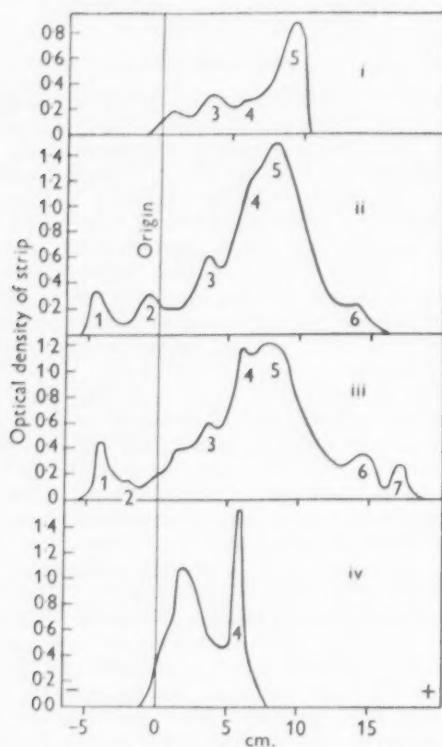


FIG. 1.—Paper electrophoresis diagrams of protein fractions from *F* solids by precipitation with ammonium sulfate. Electrophoresis was carried out for 1000 minutes in 0.05M sodium veronal buffer (pH 8.6); potential gradient 4.5 v/cm. (i), 0–25%; (ii), 25–50%; (iii), 50–70%; (iv), 70–100% saturated ammonium sulfate. The arabic numerals refer to the components of Archer and Sekhar.

0.1N NaOH with constant stirring. The pH of the mixture was not allowed to rise above 7.0. Any protein remaining undissolved at this pH was rejected. Provided that the time during which the protein-buffer mixture was kept at pH 4.5 did not exceed 30 minutes and the temperature was kept at approximately 0°, the amount of residue insoluble at pH 7.0 was very small. Washing the precipitated globulin with fresh pH 4.5 buffer tended to decrease the solubility of the product.

The solution of α -globulin was reprecipitated three times at pH 4.5 under the same conditions as those described above. The proportions of the two

citrate solutions added were adjusted to allow for the amount of caustic soda used in dissolving the protein. The final solution was then freeze-dried or preferably used at once, since the solubility of a dry sample of the protein tended to fall on storage, even at 0°.

The serum solids obtained from fresh latex by centrifuging (*C* solids) usually still contained approximately 0.5 per cent of rubber of very small particle size, which redispersed when the solids were dissolved in water. To prevent contamination of the α -globulin with this residual rubber, the *C* solids were first dialyzed in a cellophane bag against 0.01*M* trisodium citrate solution at 0° for 72 hours. The resulting solution contained the rubber in a slightly flocculated state; most of it could be removed by centrifuging at 20,000 g. The last traces of rubber were removed by the addition of ammonium sulfate

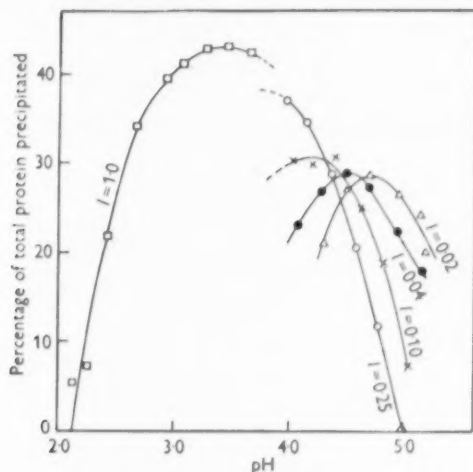


FIG. 2.—The effect of pH and ionic strength on the percentage of *F* serum proteins precipitated from sodium citrate buffer at 0°.

until the concentration was between 20 and 30 per cent saturated (a small amount of protein was also precipitated). The protein solution was then clarified by centrifuging and the α -globulin isolated as described above, starting with the precipitation by saturated ammonium sulfate.

RESULTS

Fractionation with ammonium sulfate.—Figure 1 shows the paper-electrophoresis diagrams for fractions i-iv of *F* serum solids obtained by successive precipitation with 25, 50, 70 and 100 per cent saturated ammonium sulfate, respectively. Fraction i appears to consist mainly of proteins 5 (α -globulin) and 3, in the nomenclature of Archer and Sekhar¹, but the amount of this fraction is small. Fractions ii and iii contain most of the α -globulin, but are very heterogeneous. Fraction iv consists mainly of two components, one of which is protein 4, and contains little or no α -globulin. Similar results were obtained by fractionation of the *C* solids.

Solubility of serum proteins in citrate buffer.—The over-all solubility of *F* serum proteins in citrate buffer at 0°, as a function of pH and ionic strength (*I*), is shown in Figure 2. The pH of minimum solubility is well defined at *I* = 0.02 or 0.04, but less so at higher ionic strengths. Above approximately pH 4.5, the solubility of the total protein increases with increasing ionic strength, while at lower pH values the reverse is true. The pH of minimum solubility falls from 4.7 at *I* = 0.02, or 4.5 at *I* = 0.04, to about 3.4 at *I* = 1.0. Paper-electrophoretic measurements indicated that an increase in ionic strength gave

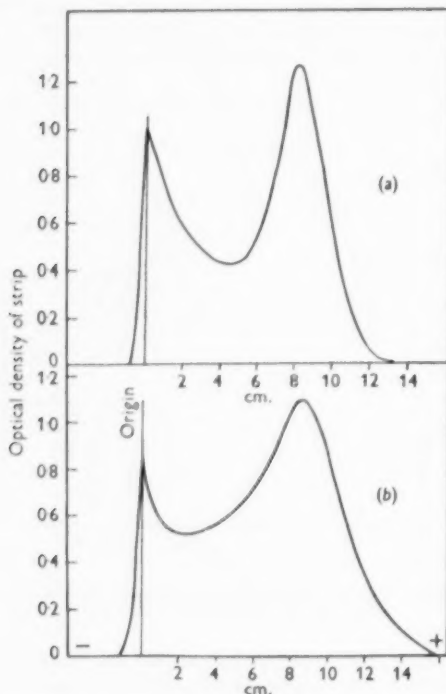


FIG. 3.—Paper-electrophoresis diagrams of α -globulin isolated from (a) *F* solids and (b) *C* solids. Electrophoresis was carried out for 1000 minutes in 0.05*M* sodium veronal buffer (pH 8.6); potential gradient 4.5 v/cm.

precipitates of increasing heterogeneity. These results apply to solutions in which the initial protein concentration was low (approximately 0.2 per cent). Further experiments at pH 4.5 showed that a gradual increase in the heterogeneity of the precipitates occurred if the initial protein-N content of the solutions exceeded 0.5 mg./ml. Use was made of these results in choosing conditions for the isolation of the α -globulin, as described in a previous section.

α -Globulin of latex serum.—Typical paper-electrophoresis diagrams for the freshly prepared α -globulin of *F* and *C* serum solids are given in Figure 3. Pronounced 'tailing' of the α -globulin spot occurs, when veronal buffer at pH 8.6 is used, owing to the ease with which the protein is adsorbed on filter paper.

The globulin of the *F* solids is indistinguishable from that of *C* solids, and the adsorption prevents ready detection of heterogeneity due to slower-moving components. However, using the Tiselius apparatus, the schlieren diagrams (Figure 4) showed the presence of two minor components in both preparations, amounting to approximately 10 per cent of the total. The faster-moving impurity is probably protein 6, detected previously by Archer and Sekhar⁴.

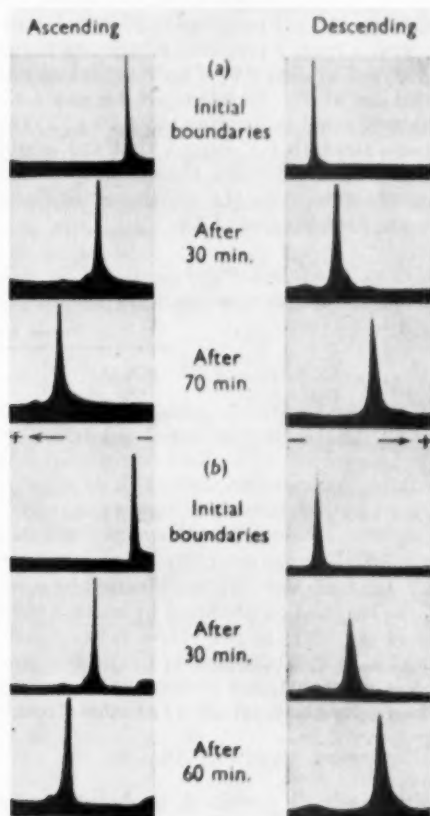


Fig. 4.—Schlieren diagrams of α -globulin from (a) *F* solids and (b) *C* solids. Tiselius electrophoresis was carried out at 0° and 5 ma, in sodium veronal buffer (pH 8.6, *I* 0.1).

Elementary analysis.—Analytical data for α -globulin (from *F* solids), after exhaustive dialysis against distilled water, are given in Table I. Also included in the table are analyses by other workers of the protein A, the main component of which is believed to be α -globulin.

Qualitative analysis of the ash showed that the chief metal present was Na (probably left from the sodium citrate buffer used in isolating the protein) with traces of Mg, K, and Ca.

Color and precipitation reactions.—Positive reactions to the following tests were obtained: biuret, ninhydrin, xanthoproteic, Millon, Sakaguchi and Adam-

kiewicz. Reactions to the Molisch and Benedict tests were negative, indicating the absence of carbohydrate. These results are in agreement with the findings of Bishop². Bondy and Freundlich³ and Kemp and Straitiff⁴, except that the last authors reported a negative Millon test.

Solubility and isoelectric range of α -globulin.—When freshly prepared, α -globulin is readily soluble in neutral or alkaline salt solutions and in acid solutions of pH less than about 3. It is insoluble in distilled water. Determinations of solubility were made over the pH range 4.1–5.9, in sodium acetate buffers of ionic strength 0.04, with a freshly prepared solution of the protein which had been exhaustively dialyzed against 0.01M sodium acetate solution. All measurements were carried out at 0°. Between pH 4.3 and 5.4, the solubility of the protein was extremely small (approximately 0.03 g./l.); very similar results were obtained at ionic strength 0.1, except that the solubility was slightly greater. On each side of these pH limits, the solubility increased very rapidly. From these solubility characteristics, the protein can be classified as a globulin with an isoelectric point in the region of 4.8.

TABLE I
ELEMENTARY ANALYSES OF α -GLOBULIN AND PROTEIN A

Element	α -Globulin (%)	Protein A	
		Bishop ² (%)	Kemp and Straitiff ⁴ (%)
N	15.7 \pm 0.1	14.0–15.1	12.7
C	52.1	—	50.7
H	6.7	—	7.3
S	0.06	—	1.32
P	<0.01	—	0.01
Ash	0.4	0.2–0.5	2.26

The effect of temperature on the solubility of the protein was examined over the pH range 5.5–8.7, the ionic strength being varied by means of sodium acetate. At $I = 0.07$, the coagulation produced by heating at 70° for 2 hours was almost complete (>94 per cent) at pH values between 5.5 and 7.0. Under the same conditions at pH 8.7, 80 per cent of the protein was coagulated. As the ionic strength was decreased, the percentage of protein coagulating decreased, becoming negligibly small (at pH 7) at ionic strengths less than 0.01.

DISCUSSION

Kemp and Straitiff⁴ isolated protein A by half-saturation of fresh latex serum with ammonium sulfate. From Figure 1, it is clear that this procedure yields a very heterogeneous fraction, containing all but one of the seven protein components detected by Archer and Sekhar¹ in fresh serum solids. The electrophoretic diagrams for fractions precipitated at other concentrations of ammonium sulfate show that the method is not suitable for purifying the α -globulin component. The difference in composition between α -globulin and Kemp and Straitiff's fraction (Table I) is particularly marked in respect of nitrogen, sulfur and ash contents, although the higher values for sulfur obtained by Kemp and Straitiff may be due in part to their preparation not being completely freed from ammonium sulfate.

The protein A isolated by Bishop² from acidified latex serum was reported to contain phosphorus, whereas α -globulin has a negligible phosphorus content

after thorough dialysis of the protein. Bishop's data for the ash content of his protein A is in good agreement with that of α -globulin. However, it is probable that the material obtained by Bishop was at least partly denatured, since its solubility was reported to be small except at very high pH values. When freshly prepared, α -globulin is readily soluble in salt solutions at pH 7, and in latex serum reconstituted from *F* or *C* serum solids.

The value of 15.7 per cent for the nitrogen content of α -globulin, the negligible phosphorus content and the negative reaction for carbohydrate indicate that it is not a conjugated protein.

SUMMARY

1. One of the two major protein components of fresh Hevea-latex serum has been isolated by an isoelectric precipitation method and the optimum conditions for the precipitation have been determined.

2. Attempts to isolate this component by fractional precipitation of the total serum proteins with ammonium sulfate gave markedly heterogeneous products.

3. A preliminary examination has been made of the purified protein. Analytical and solubility data indicate that it is a globulin lacking non-protein prosthetic groups.

ACKNOWLEDGMENTS

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REFERENCES

- ¹ Archer and Sekhar, preceding article.
- ² Roe and Ewart, *J. Am. Chem. Soc.* **64**, 2628 (1942).
- ³ Bishop, *Malayan Agr. J.* **15**, 27 (1927).
- ⁴ Kemp and Straitiff, *J. Phys. Chem.* **44**, 788 (1940).
- ⁵ Bondy and Freundlich, *Rubber Age* (N. Y.) **42**, 377 (1938).

CHROMATOGRAPHIC DETERMINATION OF RUBBER IN PLANT LATEXES *

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INTRODUCTION

Partition chromatography is a very important method of chemical analysis, particularly for the microdetermination of substances in liquids and of highly complex biological extracts¹.

Numerous authors have interested themselves in the chromatographic analysis of crude rubber or of vulcanized rubber, and have used for the purpose the method of selective adsorption in columns. In the case of crude rubber, particular attention has been paid to the possibilities of fractionating the hydrocarbon² and of determining the nonrubber ingredients, such as phosphatides³, carbohydrates⁴, proteins⁵, and colored pigments⁶. In the case of vulcanized rubber, the chief aim has been the study of certain ingredients which have escaped the more conventional methods of analysis, in particular, anti-oxygenic agents and accelerators⁷. The methods have likewise been applied to the study of the components of the latex of various plants⁸.

On the other hand, paper partition chromatography has received little study, in spite of its having the advantage of making possible the use of very small amounts of material to be analyzed; e.g., one drop (0.002–0.010 cc.) of sample, containing 0.0005 to 0.050 mg. of substance. Furthermore, with this method, measurements can be made of the partition coefficient, i.e., the ratio of the distance traveled by the substance to the distance traveled by the solvent, which is a property characteristic of any given substance.

To our knowledge, up to the present time only Banigan⁹ has applied this method to the study of benzene solutions of rubber, in which chromatographs were obtained on paper treated with methyltrichlorosilane, and cyclohexanone as the mobile phase. Banigan showed in particular that the differences found between the chromatograms of Hevea rubber and of guayule rubber depend on the mean molecular weights of the two.

In the present work, we have carried out a study of the direct chromatography of latex, with a view to effecting the separation of rubber hydrocarbon and nonrubber components and by avoiding the progressive changes which result from the extraction operations and the process of solution, to obtain facts about these substances when they are still in the same form as they are in the original plants.

LATEX AND PAPER PARTITION CHROMATOGRAPHY

The investigation was carried out with a view to studying two phases of latex: (1) the dispersed phase, with its high contents of rubber and lyophilic

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substances, and (2) the dispersing medium or serum, with its high content of hydrophilic substances. In the first part of the work, which is the subject of the present report, we devoted our attention to the separation of the dispersed phase and to the isolation of the rubber in the pure state to the greatest extent possible so that a quantitative determination could be made.

The two essential methods of paper chromatography (the method of fixed aqueous phase and the method of inverse phase partition) could not be used in this study of latex because of the complexity of the globules in suspension, as a result of which the adsorbed layer which envelops the globules gives them a mixed lyophobic character.

As a consequence, we were obliged to resort to impregnation of paper by intermediary liquids, such as formamide and propylene glycol. In addition, we utilized for the development mixtures of organic solvents saturated with water in place of the impregnating liquid itself, as is ordinarily done. As a result of having tried several mixtures of liquids, it was found that it is necessary to use two liquids having considerably different eluting powers (elutropic series of solvents).

EXPERIMENTAL TECHNIQUE

In the experiments, fresh latexes of *Ficus elastica*, kok-saghiz, and *Hevea brasiliensis*, all preserved with ammonia, were used. The *Hevea* latex was 60 per cent concentration and was diluted 100 times with 1 per cent ammonia.

In each case the tests were made with drops of latex of the same general size, i.e., 0.004–0.005 cc. The test-papers were Durieux No. 122 paper and Whatman No. 1 paper. The paper was washed, first with distilled water, then with 95 per cent alcohol. It was dried, first in air, then in an oven at 105° C for 3 hours. Immediately afterward it was impregnated by immersing strips in the impregnating liquid (1:1 formamide-methanol); the strips were finally dried in an oven at 60° C for 2 hours.

On these strips of paper were placed drops of latex 8 cm. from the lower edge. The development was carried out under cylindrical bell jars by means of a chloroform-methanol-water (10:8:5) mixture at room temperature (22° C), using the chloroform phase of this mixture. Good chromatograms were obtained after eight hours' development.

After drying, the spots were brought out by immersing the chromatograms in Oil Blue NA in alcohol solution at 45° C. It requires from four to five hours for the spots to appear. Detection of the spots by bromine is easy; all that is necessary is to keep the chromatograms in an atmosphere of bromine vapor for four hours. They are then washed with water, under which conditions the spots of rubber tetrabromide appear clearly and are permanent and white enough to stand out on the paper. On drying they disappear, but can be made to reappear as many times as desired merely by moistening the paper with water.

EXPERIMENTAL RESULTS AND DISCUSSION

In all three latexes studied, three fractions were separated by partition chromatography (see Figure 1). The fraction which is located nearest to the original location (marked by a small circle) is clearly defined in rounded form (spot *a*). The other two fractions appear in the form of bands or zones. Band *b*, the closer one to spot *a*, has a jagged outline (the middle band). The

third zone or upper zone follows the advanced front of the solvent, and it can be separated only when the paper is uniformly impregnated and when the methanol is completely evaporated.

Only the rounded spot *a* represents chromatographically a pure substance, and consequently its partition coefficient R_f can be determined. The two bands represent substances of complex nature, and it is not possible, by the method

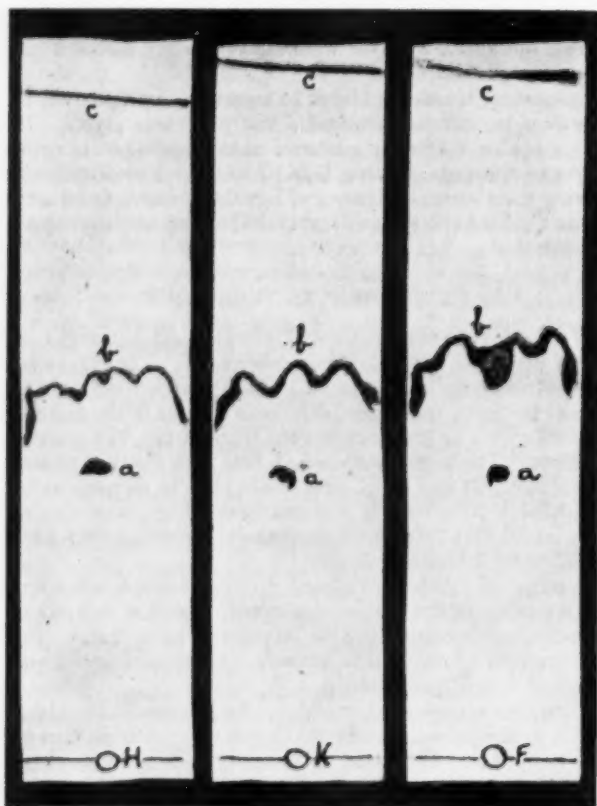


Fig. 1.—Chromatograms obtained from different plant latexes.

H *Hevea brasiliensis*
K *Kok-saghit*
F *Ficus elastica*

a Rubber hydrocarbon
b Zone of complex composition
c Front of solvent

described here, to separate the pure substances from these bands. Our purpose was, after all, to isolate the rubber hydrocarbon from the remainder of the dispersed phase, and to separate the different substances comprising the nonrubber phase would require the use of special methods.

Although Oil Blue NA can be used successfully for revealing spots, it is of no utility for further identification, for it is not specific to rubber. It was, therefore, necessary to experiment further to determine beyond doubt whether spot *a* definitely represented rubber hydrocarbon.

SOLUTION TESTS

One of the experiments carried out in the face of what is discussed above was to make solution tests of the chromatograms. The different spots, separated by cutting up the paper strips and dipping in 95 per cent alcohol to decolorize them, were treated for several hours with acetone (cold and boiling), and, after drying, the strips of paper were brought into contact with the color-

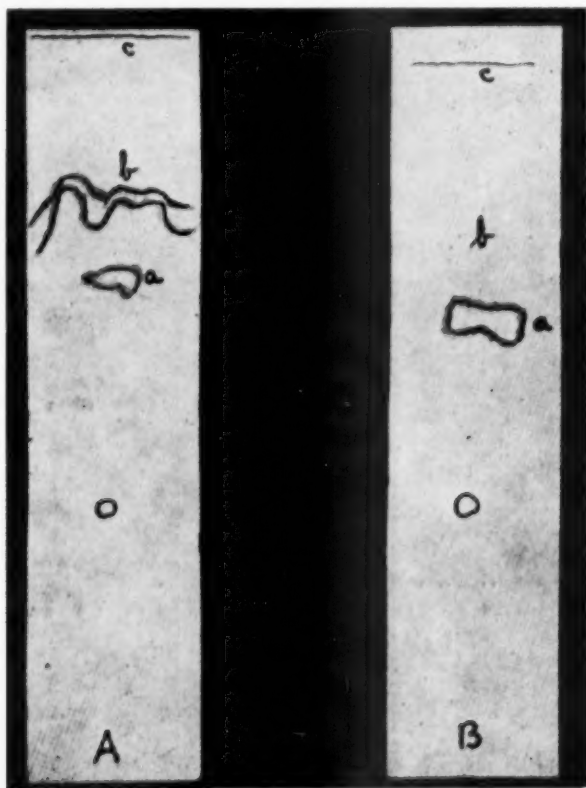


FIG. 2.—Chromatograms of Hevea latex.

Chromatogram B was kept in acetone for twenty hours and then immersed in a solution of Oil Blue NA. The zone b (nonrubber components) has disappeared by the action of the solvent.

a Rubber hydrocarbon

c Front of solvent

ing agent. It was found that only the lowest spot became intensely colored. The middle spot and the upper spot disappeared, indicating their complete solution in acetone (see Figure 2).

These chromatograms show clearly that development by partition chromatography makes it possible to separate substances soluble in acetone from substances insoluble in acetone without, however, establishing whether these insoluble substances are actually rubber hydrocarbon.

TREATMENT WITH BROMINE

In these experiments, various chromatograms were prepared and developed under the same conditions. In one of the chromatographs, the spots were brought out by means of Oil Blue NA, and this chromatogram was used as the control test. The other chromatograms were exposed to the action of bromine vapor. The strips of paper were then washed with water to eliminate excess

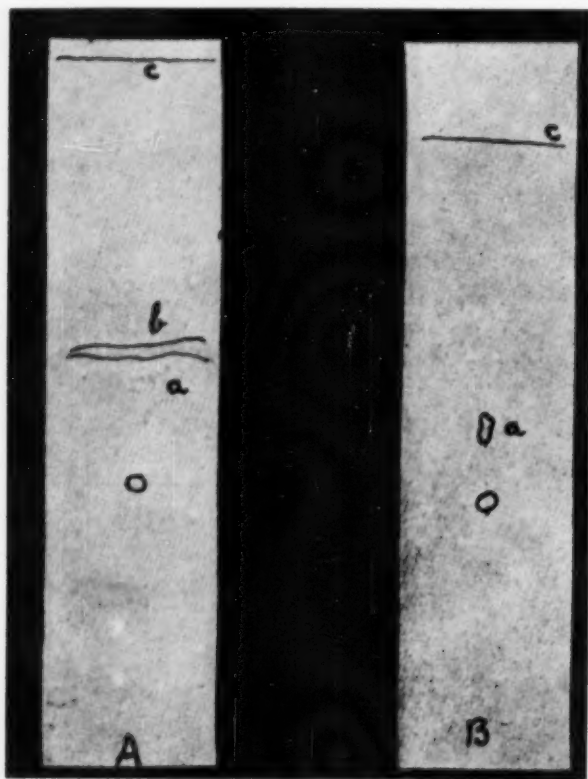


FIG. 3.—Chromatograms of Hevea latex.

A Detection of spots by Oil Blue NA B Detection of spots by bromine vapor

In this chromatogram, only the spot of rubber tetrabromide is visible.

bromine. It was thus proved (see Figure 3) that the only spots which, under these conditions, remain visible are those of the rounded form, which have resisted the action of acetone in the preceding operation. They are white, have sharply defined borders, and show the characteristic properties of rubber tetrabromide. These spots remain unaltered on heating up to 80° C, but above this temperature they commence to decompose, as evidenced by their becoming more or less pronounced yellow, with a deeper ring. This characteristic can be utilized to render the spots permanently visible.

The bands on the chromatograms are not altered by the action of bromine, and they remain invisible, but they can be rendered visible, without using any coloring agent, by simply exposing them to ultraviolet radiation, which imparts to them a yellow fluorescence. It should be added that this phenomenon bears no relation to the action of bromine.

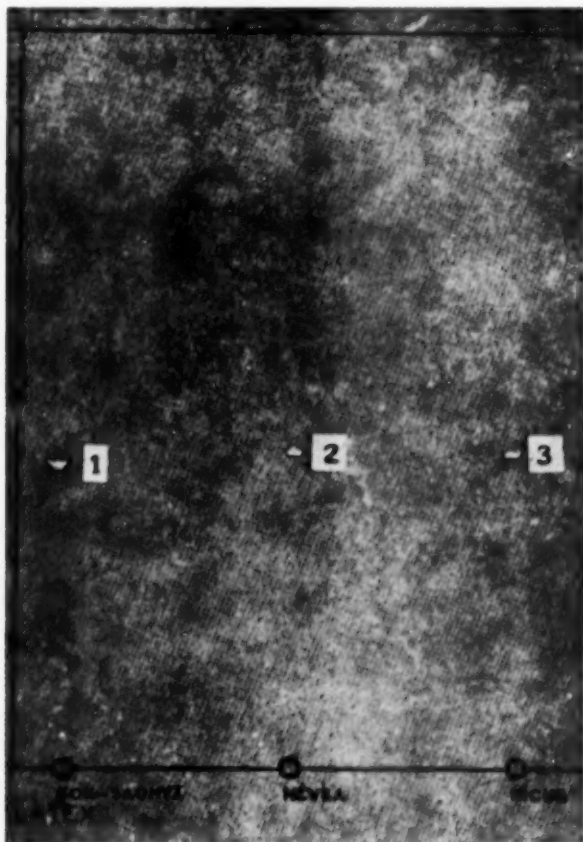


FIG. 4.—Chromatograms of different latexes. Method of detection by bromine. The white spots numbered 1, 2, and 3 represent rubber hydrocarbon.

These experiments warrant the conclusion that the rounded spots *a*, with well defined R_f , represent unquestionably rubber hydrocarbon, while the other bands represent the nonrubber components.

PARTITION COEFFICIENT OF THE RUBBER HYDROCARBON

Once having accomplished this chromatographic separation of rubber hydrocarbon direct from latex, it seemed that it might be useful to determine the partition coefficient R_f of the rubber hydrocarbon. To this end, drops of

Hevea latex on the one hand and drops of a 1 per cent benzene solution of rubber separated from the same latex on the other were developed on the same strip of paper. It was found that the R_f of the rubber hydrocarbon was the same in the two cases.

In another experiment, latexes of *Ficus elastica*, *Hevea brasiliensis*, and *kok-saghiz* were developed on the same strip of paper. The results are shown in Figure 4 and in Table 1. It will be seen that the three values of R_f are approximately the same.

To obtain an idea of the effectiveness of the method, an effort was made to find out whether, by this method, it is possible to detect the presence of rubber hydrocarbon in plant latexes containing very low percentages of rubber. Chromatographs obtained from *Euphorbia lophopoga* and from *Euphorbia*

TABLE 1
COMPARATIVE DEVELOPMENT BY CHROMATOGRAPHY OF LATEX FROM
DIFFERENT RUBBER PLANTS

Rubber plant	Development (solvent)	Paper (Whatman No. 1) Formamide impregnation of pieces 38 × 18 cm.	R_f^*
<i>Hevea brasiliensis</i>	Chloroform-methanol water (10:8:5)	—	0.43
<i>Ficus elastica</i>	—	—	0.42
<i>Kok-saghiz</i>	—	—	0.40

Time 6.5 hours. Temperature 23-24° C.

$$*R_f = \frac{\text{distance traveled by substance}}{\text{distance traveled by solvent}}$$

pulcherrima showed clearly that these latexes resemble the latexes previously examined in that they show on the one hand an intense fluorescence (from the resins) and, on the other hand, the characteristic spot of rubber hydrocarbon. The distance separating the two fractions is, however, less in the chromatograms of *Euphorbia* rubber than in those of the other rubbers.

CONCLUSIONS

Partition chromatography on paper makes possible the separation of rubber hydrocarbon from latex. This method offers a means which is both simple and rapid for determining the presence of rubber in plant latexes and for the subsequent estimation of its percentage in a given latex. The method also gives a fraction which is composed of the nonrubber components. In addition to this, the method makes possible a comparison of the partition coefficients of rubber hydrocarbon isolated from latexes of different plants.

Experiments are now in progress, the purpose of which is the application of the chromatographic method to the rapid determination of plant rubbers. By its simplicity, this method unquestionably has certain advantages in the identification of rubber in any particular flora and in studies of this hydrocarbon in its various phases of the biological cycle of the plant.

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organization for the encouragement and aid which they have given, and particularly to Jean Le Bras and Mlle. M. Boucher, whose advice has been so valuable.

REFERENCES

- ¹ For general publications on this subject, see, in particular: Lederer and Lederer, "Recent progress in chromatography", Hermann et Cie., Paris, 1949, Part I, 146 pp.; "Chromatography, a review of principles and applications", Elsevier Publishing Co., New York, 1954, 460 pp.; Block, "A manual of paper chromatography and paper electrophoresis", Academic Press, Inc., New York, 1955, 484 pp.
- ² Levi and Cajelli, *Rev. brasil. Chem.* (São Paulo) **8**, 119, 161 (1939); Cajelli, *Gomma* **3**, 1 (1939); *RUBBER CHEM. & TECHNOL.* **12**, 762 (1939); *Kautschuk* **6**, 129 (1940).
- ³ Smith, *J. Rubber Research Inst. Malaya* **14**, 169 (1953).
- ⁴ De Raftols, *Materias Vegetables* **1**, 278 (1953).
- ⁵ Rubber Research Institute of Malaya, *Annual Report for 1949-1950*, Chemical Division, p. 5.
- ⁶ Resing, *Arch. Rubbercultuur*, Extra No. 2, 33 (1953); Gee, *India-Rubber J.* **124**, 299 (1953).
- ⁷ Bellamy, Lawrie, and Press, *Trans. Inst. Rubber Ind.* **22**, 308 (1946-47); **23**, 15 (1947-48); Hamazaki, *J. Soc. Rubber Ind. Japan* **23**, 302 (1950); van Bloois, *Rubber* **8**, 75 (1952); Parker and Berryman, *Trans. Inst. Rubber Ind.* **28**, 279 (1952); *RUBBER CHEM. & TECHNOL.* **26**, 449 (1953).
- ⁸ Santos-Ruiz, *Anal. F. Lu.* **5** (1948); Bernal, *Pharmacognosia* **12**, 109 (1952).
- ⁹ Banigan, *Science* **117**, 249 (1953).
- ¹⁰ Whittenberger, *Stain Technology* **19**, 93 (1944).

PREPARATION AND USE OF CYCLIZED RUBBER AS A STIFFENING RESIN IN RUBBER *

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RUBBER-STICHTING, DELFT, HOLLAND

The condition for miscibility of low-molecular liquids is that the cohesion-energy densities should be of the same order of magnitude. The permissible difference decreases sharply as the molecular weight is increased, and a solution of equal amounts of rubber and polystyrene separates into two layers at room temperature when the concentration rises above 2 per cent, whereas low-molecular aliphatic and aromatic hydrocarbons are completely miscible. The undiluted polymers can, however, be mixed to an apparently homogeneous state on the mill if the correct mixing temperature is chosen. Presumably the extreme length of the polymer molecules allows them to be caught and dispersed separately in the stress gradient between the rolls.

That the mixture is not stable and tends to separate into the components on extension, even after vulcanization of the rubber, can be deduced from the bending of the stress-strain curve towards the strain axis—generally an indication of irreversible changes in structure for many materials. This tendency to irreversible separation, which is a disadvantage for any application, can be suppressed by the formation of primary bonds between the two polymers. There are at present three methods to produce such bonds: (1) covulcanization (if the added polymer is unsaturated); (2) mastication in an inert atmosphere; (3) graft polymerization. If a sufficient number of such bonds has been formed, the added polymer can no longer be extracted from the vulcanized compound by solvents, and the bend in the stress-strain curve has disappeared.

The relaxation spectrum of combinations of rubber and a second polymer, as shown by the rebound-temperature function, appears to consist of some simple resultant of the properties of the two component polymers, for two rebound minima are found at approximately the temperatures characteristic for the rubber and for the added polymer (Figure 1). At temperatures between these two minima, the special mechanical behavior of the combination becomes apparent, for then the added polymer reacts as an indeformable filler towards fast deformations, while during very slow deformations it may absorb mechanical energy.

If there is a large difference in flexibility of chain segments of the two polymers, the combination should react towards intermediate rates of deformation as a good approximation of a spring and dashpot model (Figure 2), with the rubber molecules as purely elastic springs and the molecules of the added polymer as viscous dashpots without elasticity. If the rubber predominates in the mixture and if the degree of interlinking is sufficiently high, there will be rubber molecules coupled parallel with every viscous molecule and Element III (Figure 2) may be neglected. The combination should then possess a high degree of retarded elasticity, with low permanent set, and should therefore be well suited for those applications for which leatherlike properties are desired.

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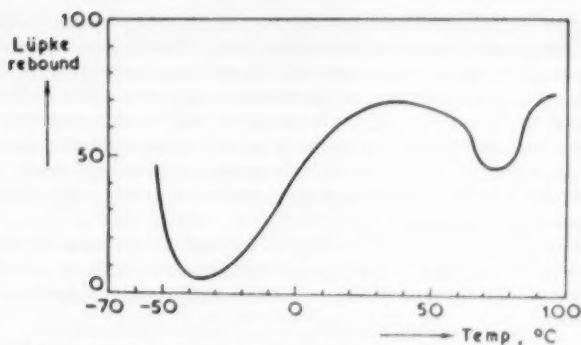


Fig. 1.—Rebound temperature curve of a compound with 50 parts of reinforcing resin per 100 parts of rubber. To the left, the minimum caused by the rubber; to the right, that caused by the resin.

A disadvantage is that the added polymer is homogeneously dispersed and bound to the rubber, so the crystallization of the rubber is depressed and the tear resistance is low.

A further consequence of the addition of a viscous polymer to rubber and covalcanization is an increase of modulus, for the slow, resin molecules are not able to follow the rate of deformation applied during the modulus determination,

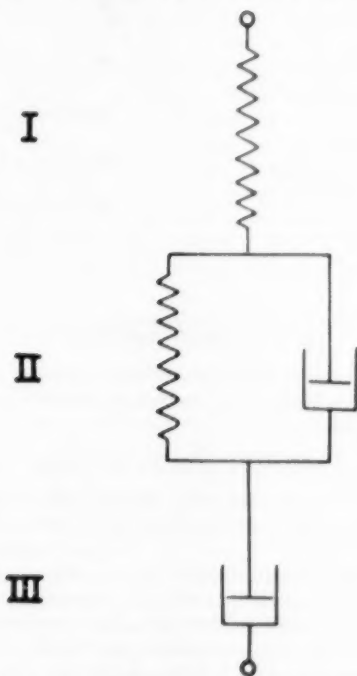


Fig. 2.—Spring and dashpot model. (I—Purely elastic: rubber; II—Retarded elastic: rubber and resin; III—Purely viscous: resin.)

and therefore a larger part of the strain must be taken up by the mobile rubber molecules; this results in an increase in stress. The increase of modulus obtained with a given amount of resin will thus depend on the mobility of the resin molecules, a property that can be conveniently characterized by the minimum rebound temperature (T_m). A graph of the modulus at 300 per cent extension of vulcanizates with 50 parts of various resins to 100 parts of rubber (Figure 3) against the T_m values of the resins (determined with the Lüpke pendulum) shows that the stiffening action of the resins can indeed be described as a function of the T_m values.

The first reinforcing resin for rubber to appear on the market was cyclized rubber prepared in solution. During the last war this product was superseded by the synthetic high-styrene resins, which have captured a large portion of the

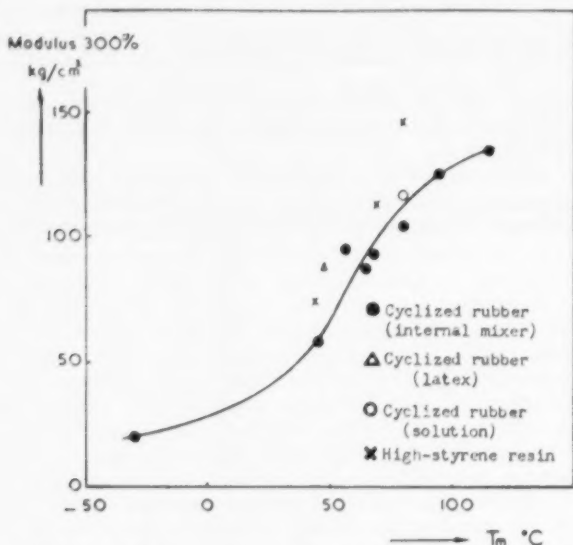


FIG. 3.—Modulus versus minimum rebound temperature (for 100 rubber-50 resin pure gum compounds).

sole and heel market. Since the War, several attempts to reintroduce cheaper forms of cyclized rubber have again drawn the attention of rubber chemists to the cyclization reaction.

CYCLIZATION OF RUBBER

The process of modifying rubber by heating with polar agents—known as cyclization—was first described by Harries¹. Subsequent experiments by Fisher², Kirchhof³ and others⁴ showed that, in general, substances that catalyze the Friedel-Crafts type of reaction also catalyze the cyclization of rubber, and, among the host of catalysts that have been advocated, are sulfuric acid, aromatic sulfonic acids, tin and aluminum chlorides, and boron trifluoride. In accordance with the modern views concerning the Friedel-Crafts type of reaction, one would expect the double bonds of the rubber to take part in any chemical changes taking place under the conditions used and, indeed, the reaction products show a decrease of unsaturation as measured by halogen or hydrohalide addition.

The most simple way to explain the physical and chemical changes observed is to assume the formation of rings, and this view has been generally accepted, although it has never been proved by the methods of organic structural chemistry⁶. If the formation of rings depends on the interaction of the double bonds of neighboring isoprene units, a certain number of these bonds—the "lone widows"—will not find a reaction partner. The residual unsaturation of exhaustively cyclized rubbers agrees with the value calculated on statistical grounds by Flory⁶. Because of these unevenly distributed unchanged isoprene units, and probably also because the chains consist of rings of varying structure, cyclized rubber does not crystallize. Cyclized rubber may thus be consistently described as a nonpolar noncrystallizing polymer, in which the molecular chains have been stiffened by ring formation.

Cyclized rubber has been prepared since 1930 on the technical scale by heating solutions of rubber with small amounts of soluble catalysts—mainly chlorine compounds of tin. The products on the market are white transparent powders which are soluble in various solvents.

In 1947 the Rubber-Stichting⁷ and the Dunlop Rubber Company, simultaneously but independently, applied for patents on a far cheaper process—the cyclization of the rubber in latex with sulfonic acid. The industrial possibilities of this process are at the moment being evaluated in Malaya on a pilot-plant scale.

There is a third possibility—the cyclization of undiluted rubber. There is evidence that this has been carried out by a number of rubber manufacturers before and during the last War for use in their own products. The process probably entails mixing a catalyst into rubber on the mill and heating the mixture in an oven for several hours at temperatures around 150° C. At the Rubber-Stichting, the cyclization of rubber in the undiluted state was investigated between 1940 and 1943 by van Royen who found that, on heating a mixture of 100 parts of low-protein crepe and 8 parts of toluene-sulfonic acid to 150° C in an oven, a strongly exothermic reaction set in, during which the temperature rose to 250° C. Substantial cyclization took place in 30 minutes with the special low-protein crepe, but the reaction was about 10 times slower with the normal grades of rubber. Repetition of this work has shown that only inhomogeneous products with medium overall degree of cyclization can be obtained by this process.

NEW CYCLIZATION PROCESS

Subsequent work at Rubber-Stichting has led to two improvements in the procedure. In the first place, it has been found advantageous to carry out the reaction in an internal mixer in order to ensure rapid, homogeneous mixing and good temperature control, and, second, the addition of small amounts of a strongly adsorbing white filler of extremely small particle size (Aerosil) has resulted in a strong accelerating effect on the reaction, which made it possible to obtain complete cyclization of even lower grades of rubber (e.g., D blankets) in not more than 10 minutes.

At first, the different preparations of toluene-sulfonic acid which were available gave widely different rates of cyclization, and the preparations, which were obtained from chemical supply firms, were either too high in price or too low in activity for economically attractive industrial operation. Then the technical grade of *p*-toluene-sulfonic acid of Hoechst & Co. was tried and found to be comparable in activity to the best laboratory preparations. Analysis has shown it to be the fairly pure monohydrate. As its price is quoted at f. 2.14 per kg. in

1000 kg. lots, it would appear that a cyclized rubber prepared with 5 to 10 parts of this acid and 5 to 10 parts of Aerosil per 100 parts of rubber would be able to compete successfully with cyclized rubber made according to the solution or the latex process and, during periods of low natural-rubber prices, with high-styrene resins.

The differences of activity between the preparations used may to a large extent be attributed to differences in water content. Drying the Hoechst acid in a vacuum of 1 mm. Hg at 120° C gave a decrease of water content from 9.5 per cent (theoretical for the monohydrate) to 3 per cent and produced a strong increase of activity, as shown by experiments on a small mill.

The catalyst is bound to the rubber during the reaction. This could be confirmed by combined sulfur determinations, for roughly 80 per cent of the sulfur in the acid used was found in this manner.

Aerosil also gave a strong accelerating effect on the cyclization in toluene solution. This is shown by the results of four experiments reported in Table I. This indicates that the accelerating effect of Aerosil may be due to heterogeneous catalysis.

TABLE I
EFFECT OF AEROSIL ON CYCLIZATION IN BOILING TOLUENE

Ingredients			Reaction time (min.)	Degree of cyclization (%)
Dry crepe solution (3.2% of rubber) (ml.)	p-Toluene-sulfonic acid (g.)	Aerosil (g.)		
200	0.50	—	20	5
200	0.50	0.50	20	34
200	0.75	—	30	28
200	0.75	0.75	30	52

Aerosil also increases the rate of reaction for the cyclization process carried out in an oven. Especially the start of the reaction is strongly accelerated, and temperatures above 300° C are easily reached in an oven at 150° C with all grades of rubber. In view of the side reactions that take place at this temperature and because of the need for bringing all double bonds in contact with the catalyst, it was preferred to carry out the reaction at a lower temperature under efficient mixing.

A large number of cyclization experiments have been carried out in our 5-l Werner Pfleiderer with the object of finding a reproducible method of operation for the production of cyclized rubber in a time no longer than that required to prepare masterbatches of rubber and high-styrene resin, and in a form which could be used by a rubber manufacturer without giving rise to processing difficulties.

In all experiments, the rubber, the acid, and the filler were put into the internal mixer together. This took about one minute. The reaction time was measured from the moment these three ingredients had been added. The starting temperature was 120 to 140° C. As the reaction is strongly exothermic, the temperature rises during cyclization and falls again after the reaction has stopped. These changes of temperature during the process were followed with the aid of a steel mercury thermometer projecting through the heating mantle of the internal mixer close to the inlet. In the normal procedure, the highest temperature should be about 180° C.

Further indications of the progress of the cyclization were obtained from the amperometer coupled to the driving motor. During the mixing period the

energy uptake should be moderate and constant, otherwise slipping is taking place and the mixing will not be efficient. If appreciable cyclization has taken place and the heat evolved has been removed by the cooling water, the energy required will increase strongly, with sharp fluctuations, showing that the mixture has stiffened. On the other hand, if the reaction has run out of control, causing the temperature to rise to 200° C, the energy required is not appreciably higher than for the empty internal mixer.

By far the best indication of the progress of the reaction, however, is the amount of gas evolved. About 3 to 4 minutes after filling the apparatus, a steady stream of gas should be produced and the flow of steam and cooling water should be regulated so as to keep the rate of gas formation constant. The gas appears to consist mainly of water vapor.

Although this method of working does not give the operator complete control of the process variables, it is possible to produce batches of cyclized rubber of the high degree of cyclization required for use as a reinforcing resin (70 to 75 per cent) in a reproducible way. It should be realized that the factors governing the heat transfer in an internal mixer of factory size are quite dissimilar to those encountered on the semitechnical scale, and therefore an increase in the scale of production will necessitate renewed experiments to find a reproducible method of production which satisfies industrial requirements.

The experiments have so far given the impression that low-protein crepe and C and D blanket crepes react faster than No. 1 smoked sheet and first-latex crepe. For the first two grades, 7 parts of acid and 5 parts of Aerosil may suffice. For the other grades, slightly more is necessary, i.e., up to 10 parts of acid and 10 parts of Aerosil.

That the reaction mixture is not dangerously corrosive to the lining of the apparatus was shown by iron determinations of the products and ingredients. The increase of iron content for a number of batches was found to be 0.009, 0.020, 0.018, 0.019 per cent iron per batch.

The cyclization was stopped after about 10 minutes by the addition of 1 part of magnesium oxide (Neoprene grade), and the product was dropped from the internal mixer after 1 minute of neutralization.

PROPERTIES OF THE PRODUCTS

The color of the products was light-to-dark brown, depending on the grade of rubber used and on the temperature reached during the reaction. When blanket crepes were cyclized at 200° C, the products appeared jet black, but even then produced light tan shades in compounds with rubber and fillers.

On cooling, the products hardened to an extent which depended on the degree of cyclization reached. Between 0 and 50 per cent of cyclization the product changed from a rubber to a leatherlike polymer, 60 to 70 per cent cyclization gives hard plastic materials, whereas the products with more than 70 cyclization are brittle. The best parameter for these mechanical properties is again the T_m value. Figure 4 shows that the whole range of T_m values of the butadiene-styrene copolymers can be copied with cyclized rubbers. Figure 5 gives the relation between this temperature and the degree of cyclization, determined from the chlorine content of the HCl adduct.

Apart from giving, by the temperature of minimum rebound, a measure of the average mobility of the polymer, the rebound-temperature curve indicates the homogeneity of the distribution of the cyclized isoprene units, since a more homogeneous product will show a sharper minimum with higher rebound values at temperatures below and above T_m . The rebound value at high tempera-

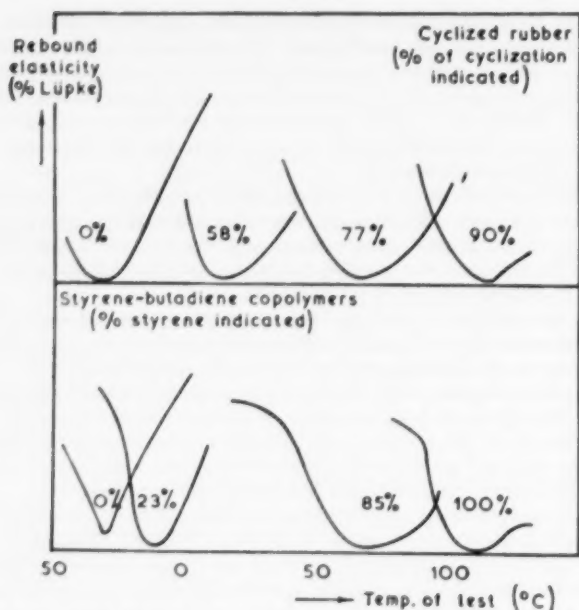


FIG. 4.—Rebound elasticity of cyclized rubber (internal mixer) and styrene-butadiene copolymer as a function of temperature.

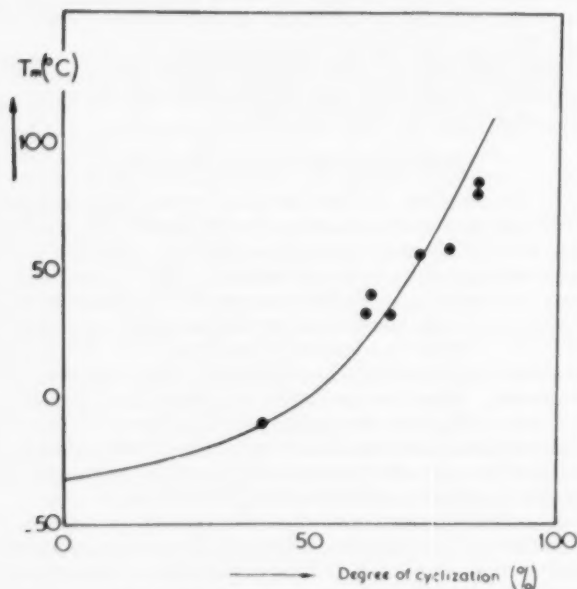


FIG. 5.—Temperature of minimum rebound elasticity as a function of the degree of cyclization for cyclized rubber (internal mixer).

tures (100° C) is an indication of the molecular weight of the product, for, if appreciable breakdown has taken place during the reaction, the unvulcanized test-piece will flow under the impact at high temperatures and the rebound value will be low.

The infrared spectra of the products were identical with the spectra of cyclized rubbers prepared in solution, with the exception of the presence of two bands indicating oxygen-containing groups. There is, of course, every opportunity for oxidation during the reaction. That oxygen is not essential for this method of cyclization follows from the very fast cyclizations obtained in boiling toluene solution (Table I) and from several experiments in the internal mixer carried out in an atmosphere of pure nitrogen, for which no appreciable decrease of rate of reaction could be observed.

As a result of breakdown during cyclization, the products may become completely soluble in benzene after reaction. This solubilization is favored by high temperatures and longer reaction times. The products prepared in nitrogen remained completely insoluble in benzene.

That hot cyclized rubber is very easily miscible with rubber is in accord with its low polarity. The preparation of 50/50 masterbatches takes 2 to 4 minutes in the 5 to 1 internal mixer or 5 to 10 minutes on the laboratory mill. If the cyclized rubber has cooled down, it should, if it has more than 50 per cent cyclization, be heated before masterbatching.

Cyclized rubbers with T_m between 0 and 20° C are still rubberlike and have very low gas permeability, comparable with that of Butyl rubber. In view of the good adhesion to rubber, this offers the possibility of using such products for impermeable layers on rubber. The high brittle point is a disadvantage, however.

Compounds of rubber and cyclized rubber of low degree of cyclization showed greatly improved resistance to ozone cracking in static tests. Since this effect may be due to stress relaxation during the test, it will be necessary to repeat these experiments using an ozone resistance test with continuously varying stress.

APPLICATIONS

Solutions.—Soluble cyclized rubbers have been used as ingredients in chemically-resistant paints, adhesive cements, printing inks, etc. The possibility of preparing highly concentrated solutions which still have a surprisingly low viscosity appears to be the main advantage of using cyclized rubber here.

Shock-resistant plastics.—A typical compound would consist of 70 parts of cyclized rubber to 30 parts of rubber as a plasticizer to decrease the brittle point, with normal amounts of fillers and vulcanizing ingredients. After press-vulcanizing in the usual way, the article taken out of the mold when hot is indistinguishable from a vulcanized rubber article, but, on cooling, it changes to a hard glossy material which resembles a plastic, and is very resistant to shocks and blows, although it can be torn or cut fairly easily. The impact resistance is high because the cyclized rubber (with a T_m slightly above room temperature) is strongly damping towards sharp deformations. Since these products have the disadvantage of softening around 60° C, the possible range of applications is limited to specialty products, such as shock helmets, golf ball covers, wash basins, etc.

Imitation leather goods.—This is by far the most promising field, and encompasses soles and heels, imitation leather cloth, footballs, etc. A typical com-

pound would consist of 70 parts of rubber with 30 parts of cyclized rubber, with white fillers and normal amounts of vulcanizing ingredients.

The main advantage of using resins in these compounds is that high hardness and stiffness can be obtained without seriously decreasing the processability. Compounds with hardness due to fillers only may show difficulties for press-curing of intricate moldings at a hardness above 70° (Shore). If the hardness is partly due to resins which soften below curing temperatures, a gain of 10 to 20° may result. The set-up of calendered sheet which is to be vulcanized in hot air or steam is also improved by resin. For instance, a leather imitation surface produced by a profiled calender may be retained during such a vulcanization. A third improvement in processability is obtained with micro-cellular compounds. Here the use of resin may obviate the after-cure in air or steam to reduce shrinkage.

Apart from the low specific gravity, which reduces the weight of the shoe, the retarded elasticity of the rubber-resin combination may be beneficial to foot comfort, for the mechanical energy returned to the floor by highly elastic compounds will be largely unpleasant and tiring.

If the cyclized rubber produced in solution is disregarded as too high in price for some of these applications, the rubber manufacturer has three stiffening resins to choose from: (1) high-styrene resins; (2) cyclized rubber masterbatch produced in Malaya from latex; (3) cyclized rubber produced in his own plant from dry rubber.

It may be of interest to point out a few differences between these three products. Some high-styrene resins have shown difficult mixing with natural rubber. This may result in laminated wear of soling if cheap nonreinforcing fillers are used. It appears that the two not completely compatible polymers are rolled out into layers on the mill, and, when used for thick soles, these layers may separate and cause extremely rapid wear. Otherwise the properties of these resins are excellent, although balanced by a fairly high price.

The cyclized rubber prepared in latex is usually mixed with latex before precipitation. The product—a masterbatch—therefore consists of hard insoluble globules imbedded in a rubber matrix. Since it is not to be expected that these globules will be dissolved homogeneously during the ordinary compounding techniques, the cyclized rubber will act as a filler which has good adhesion to rubber, but is too coarse to give an increase in tear resistance.

The cyclized rubber prepared in an internal mixer is completely compatible with rubber, and mixing is very fast. Both cyclized rubbers will be able to compete with the synthetic resins during periods of low natural-rubber prices.

ACKNOWLEDGMENT

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REFERENCES

- ¹ Harries, "Untersuchungen über die Natürlichen und Künstlichen Kautschukarten", 1919, 2.6.
- ² Fisher, *Ind. Eng. Chem.*, 19, 1325 (1929).
- ³ Kirchhof, *Kolloid-Z.*, 30, 183 (1922).
- ⁴ Stevens and Miller, *RUBBER CHEM. & TECHNOL.*, 12, 556 (1939).
- ⁵ Stevens and Miller, *RUBBER CHEM. & TECHNOL.*, 12, 556 (1939); van Veersen, *RUBBER CHEM. & TECHNOL.*, 24, 957 (1951).
- ⁶ Flory, *J. Am. Chem. Soc.*, 61, 1518 (1939).
- ⁷ Gordon, *Brit. Pat.* 634,879 (1950).

OXIDATIVE STRESS RELAXATION OF NATURAL RUBBER VULCANIZED WITH DI-TERTIARY-BUTYL PEROXIDE *

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It has been shown by Farmer and Moore¹ that natural rubber can be vulcanized with di-*tert.*-butyl peroxide (DTBP). Presumably the free radicals formed by the unimolecular decomposition of the peroxide abstract some of the more labile (e.g., α -methylene) hydrogen atoms, leading to direct C-C cross-links between the rubber molecules, with *tert.*-butanol and acetone as the main reaction products.

This preliminary communication presents some of the results of an investigation of the oxidative stress relaxation of the following types of DTBP vulcanizates.

(A) First grade pale crepe, DTBP, and carbon black (MPC) mixed on the mill and vulcanized in a press. The carbon black was added to minimize the deleterious effect of impurities.

(B) Purified rubber vulcanized: (1) in aqueous heating media; (2) in the press; (3) in DTBP vapor.

(A) In Figure 1 is plotted on a logarithmic scale the relaxation curves for a vulcanizate with 20 per cent MPC black vulcanized for 15 minutes at 160° C and relaxed in air at 90–140° (modulus 2.57 kg./cm.² at an extension ratio of 1:2). A rapid initial rate of relaxation, due primarily to peroxidic reaction products, was eliminated by preheating the samples in vacuo for 30 minutes at 150°. This treatment also serves to remove the physical relaxation. From the relaxation curves shown in Figure 1, an energy of activation of 22.7 kcal. is calculated for the relaxation process. The same relaxation rates are obtained when only 5 per cent of MPC black is used. The relaxation rate is nearly inversely proportional to the initial modulus of the sample, corresponding to a rate of oxidation nearly independent of the degree of vulcanization. With no preheating in vacuo, there would also, in addition to the normal initiation of oxidation chains by hydroperoxide decomposition, be an initiation by some nonvolatile peroxidic substances formed during the vulcanization process, the amount of which will depend on the degree of vulcanization.

When approximately 75 per cent of the stress is relaxed, the relaxation curves of the preheated samples start deviating from linearity, apparently mainly because of the consumption of natural antioxidant in the oxidation. A closer examination shows that this occurs somewhat earlier when the degree of vulcanization is higher, corresponding to a consumption of natural antioxidant during vulcanization with DTBP. Acetone extraction of the samples before heat treatment in vacuo has practically no influence on the relaxation rates. The antioxidants left are, therefore, probably proteins and possibly some of the normally extractable antioxidants which have been chemically bound to the rubber during the vulcanization.

* Reprinted from the *Acta Chemica Scandinavica*, Vol. 9, No. 6, pages 1024–1026 (1955).

The rate of cross-linking was measured by subjecting the relaxing sample intermittently to a small additional stress and measuring the corresponding increase of elongation. This method gives (as confirmed by tests on a pure-gum sulfur vulcanizate) the same value for the rate of cross-linking as do the ordinary intermittent stress relaxation measurements on a separate sample, and the former method seems to have certain advantages. The rate of cross-linking was found to be 25–30 per cent of the rate of scission in the whole temperature range studied, i.e., with the same energy of activation. If the samples were acetone-extracted, however, the rate of cross-linking was 45–50 per cent at 90° and reached 25–30 per cent at the higher temperatures. This may be a combined effect of the acetone-extractable substances acting as a plasticizer and the cross-linking capacity of the carbon black, although there was only a small difference between the effect when 20 per cent and when 5 per cent MPC black was used.

(B) In order to avoid the use of additives, such as carbon black, a purified rubber was used in the following experiments, in which the effect of the degree and mode of vulcanization and of the pretreatment of the samples on their

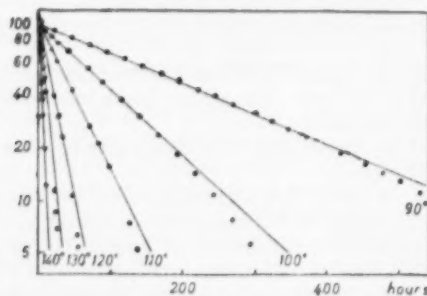


FIG. 1.—Relaxation curves. The ordinate indicates the percentage of the original stress; the abscissa the time in hours.

oxidation and relaxation behavior was studied. The rubber was extracted from first grade pale crepe by a modification of the method of Bloomfield and Farmer² and should, according to this, be free of the "oxide fractions". The nitrogen content was about 0.035 per cent. Films 0.05 mm. thick were prepared from solution and vulcanized at 150° for 30 minutes.

By vulcanization in distilled water in an oxygen-free atmosphere, followed by extraction with acetone, the peroxidic material formed in the samples was still sufficient to be the dominating oxidation chain initiator at the beginning of the relaxation process. This peroxidic material seems to be chemically combined with the rubber, and can preferably be destroyed by heating the sample in vacuo. Results of experiments on samples in which such a more nearly complete removal of the peroxidic substances has been carried out will be published later. In the experiments described here, a relatively mild heat treatment of 10 minutes at 120° was used. This reduced the initial relaxation rate by approximately 50 per cent. The hatched area I shown in Figure 2 covers the relaxation curves (on a linear scale) of eight vulcanizates of modulus varying from 2.4 to 4.7 kg./cm.² (at an extension ratio of 1:25), the upper curve corresponding to the higher modulus. Relaxation was carried out in dry oxygen at 90°. Without preheating, a modulus of 2.7 gave the relaxation

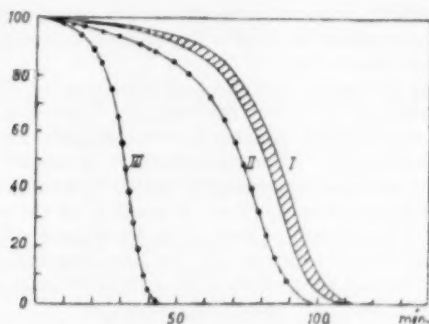


FIG. 2.—Relaxation curves. The ordinate indicates the percentage of the original stress; the abscissa the time in minutes.

curve II. The reproducibility was very good. Several factors play a part in determining the dependence of the curves I on modulus: the dependence of the concentration of the peroxidic substances on the degree and conditions of vulcanization, the dependence of the oxidation rate on this concentration, and the consumption of natural antioxidant as a function of degree and mode of vulcanization.

The curve III represents a preheated sample of modulus 2.7 kg./cm.^2 relaxed at 100° . The activation energy calculated from the relaxation curves differs little from the value obtained for the inhibited relaxation of the whole-crepe vulcanizates described above. In accordance with the network theory, the amount of oxygen absorbed (preliminary gravimetric measurements) at 99 per cent relaxation is proportional to the degree of vulcanization. There was no measurable cross-linking at 90° .

Figure 3 shows the relaxation (at 90°) of samples vulcanized (1) in water and with 5 per cent stearic acid in the rubber; (2) in 2 *N* sodium hydroxide and (3) in pure DTBP vapor. (The ranges of moduli covered by the areas shown are not as large as in Figure 2.) Apparently the stearic acid promotes the deactivation of the proteins, giving a less inhibited reaction, whereas the addition of sodium hydroxide to the water mainly serves to reduce the water con-

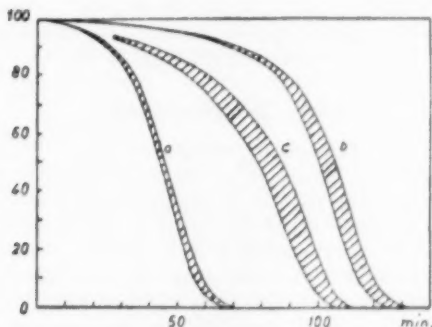


FIG. 3.—Relaxation curves. The ordinate indicates the percentage of the original stress; the abscissa the time in minutes.

centration in the rubber, thus reducing the rate of deactivation by the DTBP. So efficient is this osmotic effect that a dry sample vulcanized in a press gave exactly the same relaxation curve.

It is interesting to observe the effect of incorporating 0.2 per cent copper stearate in the samples of (1) before preheating. There is a marked reduction of the initial relaxation rate, presumably because of a more complete destruction of the peroxidic substances. This marked effect of copper stearate indicates that these peroxidic substances are largely rubber hydroperoxides. They may be formed in the vulcanization reaction, or possibly at the moment the cooled sample (with a certain amount of free radicals) is removed from the press or the autoclave and exposed to the air. In the later stages, however, the catalytic and antioxidant-inactivating effect of the copper stearate becomes apparent, giving a much faster rate than uncatalyzed samples.

By the vulcanization in DTBP vapor for 30 minutes at 150°, the rubber became seriously overvulcanized at the surface. As should be expected, the curves (c) in Figure 3 show that the antioxidant-free stage is reached comparatively late in this case.

This investigation is being completed and extended to comprise accurate oxygen absorption measurements in order that the relation between this pure scission reaction and the detailed shape of the relaxation curve may be studied.

ACKNOWLEDGMENTS

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REFERENCES

- ¹ Farmer and Moore, *J. Chem. Soc. (London)*, 1951, p. 142.
- ² Bloomfield and Farmer, *Trans. Inst. Rubber Ind.*, 16, 69 (1940).

INFLUENCE OF INHIBITORS ON THE OXIDATION OF RUBBER SOLUTIONS *

E. N. NOVIKAVA

The works of Dogadkin¹, Kuzminskii², and other investigators have established the fact that a fundamental factor in the aging of rubber is its oxidation by atmospheric oxygen. From this point of view the study of the influence of the composition, structure, and polarity of chemical compounds as inhibitors of rubber oxidation is of importance.

Koshalyov³ and Yasenкова showed that secondary amines used as antioxidants are consumed during the aging of rubber. Kuzminskii⁴ describes the mechanism of the action of inhibitors as a reaction between their molecules and the rubber peroxide radicals, leading to rupture of the oxidation chain and consumption of the inhibitor during oxidation. Here the oxy compounds destroy the stable peroxides, while the amino compounds react with the rubber peroxide radicals. Yarmolenka and the author have described a sorption theory of the mechanism of action of antioxidants, which is based on the fact that nearly all antioxidants are, to some degree, polar compounds and consequently are solvated by rubber at the double bonds, thus preventing oxidation of the rubber by oxygen. The induction period is the time of desorption of the molecules of antioxidant.

In a previous study⁵ the author showed the influence of the polarity of phenols on their capacity to inhibit rubber oxidation. It is known that the polar properties of chemical compounds are determined by the nature and distribution of the molecular groups. In a work of Kutanav⁶, the influence of the nature of functional groups which change the polarity of organic acids on the adsorption of these acids by mixed mediums was observed. Assuming that the structure and polarity of inhibitors have particular importance for their inhibition effect, by influencing the mobility of the hydrogen they contain, the authors undertook a systematic study of special classes of chemical compounds with respect to their influence on rubber oxidation as related to structure and polarity. The results of a study of the influence of the composition and structure of chemical compounds containing amino groups (diamines, carbazides, carbazones, azo compounds) on rubber oxidation are presented in this study.

EXPERIMENTAL PART

The inhibiting effect of various groups of chemical compounds was studied with purified pale crepe hydrocarbon. The rubber hydrocarbon was oxidized in a xylene solution with dry oxygen at 70° C in the presence of antioxidants, in darkness. The antioxidants were added to the rubber-xylene solution in equimolecular amounts, namely, 0.01 gram-molecule of antioxidant per 100 grams of pure hydrocarbon. In cases where the antioxidant did not dissolve immediately in the xylene solutions, it was first dissolved in alcohol or dioxane, and then a small volume (1 ml. of alcohol per 50 ml. of rubber solution) was

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from *Vestsi Akademii Navuk Belaruskai S.S.R.* 1954, No. 2, pages 62-72.

added to the rubber solution. In order to calculate the influence of alcohol or dioxane on the oxidation of rubber in solution, we made simultaneous control experiments without antioxidant, but with alcohol added in the amount necessary for addition of the antioxidant. A 6 per cent solution of rubber hydrocarbon was oxidized in closed glass vessels described in a previous study⁷. The solution was agitated during oxidation, favoring closer contact between the solution and oxygen. The relative viscosity of the oxidized solutions was measured in order to control the oxidation during the process.

OXIDATION OF RUBBER IN THE PRESENCE OF AMINES

Compounds which contain two amino groups in each molecule with the diphenyl nucleus in *para*-position or which are distinguished by the nature and distribution of their substituent groups, were chosen for the study of the inhibition by aromatic amines of the oxidation of rubber. By relating the activity of inhibitors to the polarity of their molecules, we hoped to determine how the nature of the substituent groups influences the reaction of diamines as rubber antioxidants.

As the data in Table 1 show, the relative viscosity of rubber solutions oxidized in the presence of tolidine is considerably greater than that of solutions oxidized in the presence of benzidine. When two hydrogen atoms of the aromatic ring in benzidine are substituted for two methylene groups arranged in *ortho*-position with respect to the amino group, the antioxidation activity of tolidine is reduced, in comparison with benzidine. If the reactivity of Tonox and benzidine is calculated from the data of relative viscosity, then the latter is somewhat more active than the former. The relatively weaker inhibiting action of Tonox can evidently be explained by the presence of a CH_2 group in the molecular chain, which influences the polarity of all the molecules.

Comparing the relative viscosity of rubber solutions oxidized with added Oxynone and benzidine, we observed the great inhibiting action of Oxynone. The Oxynone molecule, like that of Tonox, is composed of two benzene rings and two substituent amino groups, while there is a NH group in the chain of diaminodiphenylamine; furthermore, one of the two amino groups is in *ortho*-position with respect to the amine group. All these factors increase the inhibiting action of Oxynone in comparison with Tonox and benzidine. In order to confirm the effectiveness of the action of the indicated diamines in the presence of accelerators of rubber oxidation, we investigated the oxidation of rubber solutions containing added iron palmitate.





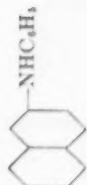
The relative viscosities of oxidized rubber solutions listed in Table 1 show that the activity of benzidine, Tonox and tolidine is considerably reduced in the presence of iron palmitate. As for Oxynone, its inhibiting action is not changed at all under these conditions.

The influence of iron palmitate on Neozone D, chosen for purposes of comparison, is less than that of Oxynone, as was shown in a previous study⁷.

The measurements of the relative viscosity of oxidized rubber solutions in the presence of amines, as shown in Table 2, indicate the influence of the nature and distribution of the substituent group in the benzene ring on the effectiveness of antioxidants.

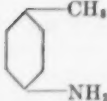
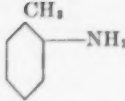
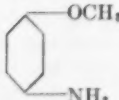
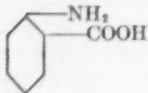
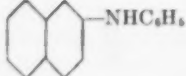
p-Toluidine and *p*-anisidine differ only in the nature of the substituent group; hence the higher activity of *p*-anisidine is due to the OCH_3 substituent group. With the same *p*-position, the OCH_3 substituent group has a decisive influence on the antioxidation effect of the amines indicated in comparison with

TABLE 1
RELATIVE VISCOSITY 0.6 PER CENT SOLUTION OF RUBBER OXIDIZED IN PRESENCE OF DIAMINES AT 70° C

Antioxidant	Structural formula of antioxidant	Melting point (° C)	Relative viscosity of rubber solution at 20° C		Remarks
			Oxidized with anti-oxidant	Oxidized with anti-oxidant + 0.05% iron	
<i>p,p'</i> -Diaminobiphenyl (benzidine)		127.5-128	5.27	3.26	Viscosity of original solution before rubber oxidation, 11.3
3,3-Dimethylbenzidine (tolidine)		128-129	4.13	2.87	Oxidation period of solution in presence of antioxidant, 5 hours
<i>p,p'</i> -Diaminodiphenylmethane (Tonox)		92-91	5.10	2.90	
2,4-Diaminodiphenylamine (Oxyne)		116	7.27	7.23	Oxidation period of solution in presence of antioxidant and iron palmitate, 3 hours
Phenyl-2-naphthylamine		108	9.92	7.18	
Without antioxidant	—	—	3.33	2.54	

the CH_3 group. *o*-Toluidine and *o*-aminobenzoic acid likewise differ only in the nature of the substituent groups, which are in *o*-position to the amino group. *o*-Aminobenzoic acid does not inhibit the oxidation of rubber, owing to the negative effect of the carboxyl group, which is in *o*-position with respect to the amino group, as well as to the part played by the so-called ortho-effect. Thus, in the same *o*-position, the substituent carboxyl group has a negative effect on aminobenzoic acid as an antioxidant, in contrast to the CH_3 group in *o*-toluidine.

TABLE 2
RELATIVE VISCOSITY OF 0.6 PER CENT RUBBER SOLUTION
OXIDIZED IN PRESENCE OF AMINES AT 70° C

Antioxidant	Structure of antioxidant	Melting point (° C)	Relative viscosity of rubber solution oxidized in the presence of antioxidants	Remarks
<i>p</i> -Toluidine		44-45°	7.43	Viscosity of original solution, 10.84
<i>o</i> -Toluidine		-16.3°	7.47	
<i>p</i> -Anisidine		57.2°	8.59	
<i>o</i> -Aminobenzoic acid		144-5°	6.46	
Neozone D			10.70	
Without antioxidant	—		6.66	

RUBBER OXIDATION IN THE PRESENCE OF AZO COMPOUNDS

Azo-compounds, which contain amine and methyl groups, were studied in connection with the influence of the nature and distribution of substituent groups on the activity of inhibitors of rubber oxidation.

Studies of rubber oxidation in the presence of azo compounds (Tables 3 and 4) show that the azo compounds examined inhibit the oxidation of rubber. On the basis of these data, azo compounds can be classified in the following order according to their inhibiting action on oxidation: *p*-aminoazobenzene, dimethylaminoazobenzene-*o*-carboxylic acid, dimethylaminobenzene, and azobenzene. Bismarck brown dye did not entirely dissolve in a rubber-xylene solution;

TABLE 3
RELATIVE VISCOSITY OF 6 PER CENT SOLUTION OF RUBBER OXIDIZED IN
PRESENCE OF AZO COMPOUNDS AND IRON PALMITATE AT 70° C









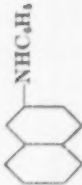
Antioxidant	Structure of antioxidant	Relative viscosity of rubber solutions at 20° C		Remarks
		Oxidized with anti- oxidant	Oxidized with anti- oxidant and 0.05 per cent iron	
Azobenzene		5.23	2.73	Original viscosity of solu- tion before oxidation, 13.5
p-Aminoazobenzene		7.42	3.76	Oxidation time with anti- oxidant, 10 hours
Diazoaminobenzene		2.66	3.52	Oxidation time with anti- oxidant and iron, 6 hours
Dimethylaminoazobenzene- o-carboxylic acid		6.013	3.00	
Without antioxidant	—	4.65	2.44	

TABLE 4
RELATIVE VISCOSITY OF 0.6 PER CENT RUBBER SOLUTION OXIDIZED
IN THE PRESENCE OF AZO-COMPOUNDS AT 70° C

Antioxidant	Structure of antioxidant	Melting point (° C)	Relative viscosity of rubber solutions at 20° C	Remarks
<i>p</i> -Aminooazobenzene		125-127°	7.13	Viscosity of original rubber solution before oxidation, 9.52
Dimethylaminoazobenzene		116-117°	6.07	Oxidation time 5 hours
Dimethylaminoazobenzene- <i>o</i> -carboxylic acid (methyl red)		—	6.67	Antioxidants were first dissolved in alcohol and then added to rubber solution
Triaminoazobenzene (Bismarck brown)		—	6.57	Bismarck brown was completely insoluble
Phenyl-2-naphthylamine		107-108°	8.41	
Without antioxidant	—	—	4.73	

nevertheless, it proved to be a more effective inhibitor of rubber oxidation than dimethylaminoazobenzene.

As the data of relative viscosity show, the activity of azo compounds during the oxidation of rubber in solution varies according to the nature of the substituents in the ring bound by an azo group. Azobenzene does inhibit oxidation, although only slightly. The presence of the phenylazo group in the ring in *para*-position to the amino group increases greatly the activity of the antioxidant *p*-aminoazobenzene.

The dimethylamino group has a weaker effect than the amino group on the action of an inhibitor. If the relative viscosities of rubber solutions oxidized with added azobenzene and dimethylaminoazobenzene are compared, the latter is more active; that is, it has a stronger effect on the inhibition power of an antioxidant in this case. At the same time, the data on the relative viscosity of rubber solutions oxidized with *p*-aminoazobenzene and dimethylaminoazobenzene show that the latter is less active than the former. Thus, the amino group has a stronger effect on the inhibition power of the compounds indicated than does the dimethylamino group.

The inhibition action of dimethylaminoazobenzene-*o*-carboxylic acid is greater than that of dimethylaminoazobenzene. This fact can be explained by the presence of a carboxyl group in the aromatic ring in *ortho*-position with respect to the azo group, which, one must assume, changes the polarity of the entire molecule. Our studies of the oxidation of rubber solutions containing diazoaminobenzene showed that the latter does not inhibit the oxidation of rubber, but rather initiates oxidation more rapidly. If rubber is oxidized in the presence of iron palmitate, diazoaminobenzene proves just as effective an antioxidant as *p*-diazoaminobenzene, and more effective than azobenzene. It is known⁸ that diazoamino compounds form salts with metals; consequently it seems that diazoaminobenzene, upon uniting with iron, lowers the catalytic activity of the latter.

INFLUENCE OF CARBAZONES AND CARBAZIDES ON THE OXIDATION OF RUBBER

The carbazides and carbazones chosen in this work as antioxidants were added, in small volumes of alcohol or dioxane, to a solution of rubber in xylene. The rubber samples containing these antioxidants were oxidized for 3, 5, and 6 hours. Measurement of the relative viscosities of these solutions showed that the inhibitory effect of phenylsemicarbazide and diphenylcarbazine is greater than that of Neozone D, which is so widely used in industry.

Comparison of the data on relative viscosity presented in Table 5 shows the relatively great inhibiting effect of phenylsemicarbazide. This strong effect is evidently attributable to the relatively long open molecular chain and the number of amino groups. The lower antioxidant activity of diphenylcarbazine in comparison with diphenylcarbazine can be explained satisfactorily by the presence of the amino groups, which have a relatively high antioxidant power, by a double bond system. As is evident from the data in Table 5, diphenylthiocarbazon also is an effective antioxidant. The different effects of these compounds on the oxidation of rubber is explained by their molecular structures. Diphenylthiocarbazon contains a polyvalent sulfur atom, which evidently determines the oxidation capacity.

To relate the activity of an inhibitor to its structure, it was of interest to investigate to what extent a more complex molecule of similar type influences

TABLE 5
RELATIVE VISCOSITY OF 0.6 PER CENT RUBBER SOLUTION OXIDIZED IN THE
PRESENCE OF CARBAZONES AND CARBAZIDES AT 70° C

Antioxidant	Structure of antioxidant	Melting point (° C)	Relative viscosity of rubber solutions at 20° C			Remarks
			Oxidized 3 hours	Oxidized 6 hours	Oxidized 5 hours	
Diphenylthiocarbazon		—	3.74	3.28	—	Viscosity of original rubber solution for data of type IV and V, 7, 8; for type VI, 11, 62
Diphenylcarbazon		182°	6.83	4.85	8.26	Antioxidant was added to solution, 0.01 mole per 100 g. of rubber for type IV and VI, and 0.05 mole per 100 g. for type V.
Diphenylcarbazine		156-158°	7.67	6.59	8.81	
Phenylsemicarbazide		172°	—	—	9.04	For data of type V anti- oxidant was added in alcohol, and for other types in dioxane
Phenyl-2-naphthylamine (Neozone D)		108°	6.51	5.62	8.30	
Without antioxidant	—	—	5.06	4.51	6.92	

TABLE 6
RELATIVE VISCOSITY OF 0.6 PER CENT SOLUTION OF RUBBER OXIDIZED AT 70° C

Antioxidant	Structure of antioxidant	Melting point (° C)	Relative viscosity of rubber solutions at 29° C		Remarks
			Oxidized with anti-oxidant, Oxidation time 5 hours	Oxidized with anti-oxidant and oxidant, 0.05 per cent iron, Oxidation time 3 hours	
Azobenzene		68°	12.92	4.87	Viscosity of original solution 17.00
2-naphthol		122-123°	15.13	12.24	
Sudan I		134-135°	13.47	5.90	
Sudan III		195°	14.76	12.87	
Without antioxidant	—		11.03	4.32	

the inhibitory action of antioxidants. For this purpose the oxidation of rubber in the presence of Sudan I, Sudan III, and (for comparison) 2-naphthol and azobenzene, was studied.

As the data in Figure 6 show, Sudan I and Sudan III inhibit the oxidation of rubber; however, the inhibitory action of 2-naphthol is greater. The relatively low activity of Sudan I and III can be explained by the *ortho*-position of the OH group with respect to the azo group.

If we compare the inhibition action of Sudan I and III, the latter is more effective, owing to the length of its molecular chain.

CONCLUSIONS

1. The nature and distribution of substituent groups (NH_2 , $\text{N}(\text{CH}_3)_2$, CH_3 , OCH_3 , COOH) influences the relative activity of amines as rubber antioxidants.
2. Azo compounds fall in the following order of their inhibiting action on rubber oxidation: *p*-aminoazobenzene, dimethylaminoazobenzene-*o*-carboxylic acid, dimethylaminoazobenzene, azobenzene.
3. Phenylsemicarbazide is a more effective antioxidant than Neozone D.
4. Diazoaminobenzene and diphenylthiocarbazon do not inhibit the oxidation of rubber, but initiate it quite rapidly.
5. Sudan I and III inhibit the oxidation of rubber solutions, but less than does 2-naphthol.

REFERENCES

1. Dogadkin, "Khimia i Fizika Kauchuka", 1947.
2. Kuzminskii and Leshnev, "Khimia i Fiziko-Khimia Vysokomol. Soedinenii".
3. Koshalyov and Yashkova, *Pratsky Mosk. ITK&T im. Lomonosova*, Vol. I, 1948.
4. Kuzminskii and Angert, *Doklady Akad. Nauk S.S.S.R.*, Vol. 82, No. 5 (1952).
5. Yarmolenko and Novikava, *Vestsi Akad. Nauk Belarus. S.S.R.*, No. 4, 1952.
6. Kutanav, *Vestsi Akad. Nauk Belarus. S.S.R.*, No. 4, 1953.
7. Novikava, *Akad. Nauk Belarus. S.S.R.*, No. 5, 1952.
8. Karer, "Kurs Organichnoi Khimii", Moskva, 1938.

ELECTRICAL CONDUCTIVITY EXPERIMENTS WITH HIGH-ABRASION FURNACE BLACK-LOADED NATURAL RUBBERS *

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INTRODUCTION

This work was carried out in 1952 and arose from the interest shown by many rubber companies in the manufacture of articles having electrical resistivities in the antistatic and conductive categories. A survey of medium and small companies suggested that basic information about the possible magnitude of variation between the resistivities of nominally identical articles was limited, and it seemed likely that there was a general tendency to underestimate the variations to be expected. Since commercial products form too wide a field for the study of such a subject, it was decided to concentrate on laboratory vulcanizates in an attempt to gain some idea of the variability inherent in processing when such processing is carried out with every precaution to minimize experimental error.

It has often been reported that milling time is a potent source of variation of resistivity of vulcanizates, although detailed results are scanty, and this factor is the primary subject of Part 1 of the present work. Also investigated in Part 1 are certain other basic sources of error. Part 2 consists of an evaluation of two methods of testing resistivity and gives an indication of the extent to which variability outside control by careful technique exists. Part 3 is a simple demonstration of the effect of compressive flexing on electrical resistivity of vulcanizates.

I. EFFECT OF TIME OF MILLING

Four batches (A, B, C, D) each of the following composition were mixed, a masterbatch of everything except the pine tar and carbon black being employed. The pine tar and carbon black were added to a strictly controlled time/temperature cycle. Half of each batch was remilled for a further five minutes.

Smoked sheet rubber	100
Stearic acid	2.5
Zinc oxide	5
C.B.S.	0.5
Sulfur	2.5
Pine tar	4.5
HAF black	50

A nine-cavity mold to produce specimens with brass-bonded electrodes¹ was used, with a cure of 40 minutes at 138° C, which is known to be somewhat above

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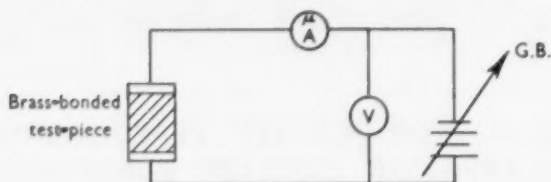


Fig. 1.

optimum for the formula and therefore free from the marked effects of undercure. The order of curing was randomized to spread chance errors as far as possible. Since mixing and remilling was done on the same day, vulcanizing the following day, and testing the third day, a further source of chance error is eliminated. The vulcanizates were made from blanks cut to a predetermined weight, and all sheets of rubber were taken off the mill as nearly as possible to

TABLE I

Mold cavity no.	Batch			
	A	B	C	D
1	10	12	10	20
2	20	10	8	18
3	12	8	20	23
4	15	10	8	25
5	10	12	12	35
6	10	15	12	45
7	20	30	15	20
8	10	10	15	25
9	15	8	8	5

(Not remilled. Not heat-treated.)

the same thickness, this thickness being such as to give the minimum flow in the mold. Vulcanizates were pushed from the mold by means of a die so as to avoid distortion and were cooled on a zinc topped bench. Storage of stocks and vulcanizates was in a temperature and humidity controlled atmosphere (21° C and 60 per cent relative humidity), and testing was carried out under the same conditions. One set of vulcanizates was tested untreated except for

TABLE II

Mold cavity no.	Batch			
	A	B	C	D
1	25	35	20	30
2	75	45	30	35
3	35	25	25	25
4	35	25	20	20
5	25	20	20	25
6	20	30	35	25
7	60	35	35	60
8	50	40	45	40
9	50	60	40	40

(Remilled not heat-treated.)

TABLE III

Mold cavity no.	Batch			
	A	B	C	D
1	8	8	10	10
2	10	8	7	12
3	8	8	7	11
4	11	6	8	11
5	8	8	8	11
6	8	10	7	10
7	11	11	10	11
8	9	11	11	10
9	11	11	10	11

(Not remilled. Heat-treated.)

gentle cleaning of the surface with an acetone moistened cloth; the other set was heated for one hour in air at 100° C, and then allowed to cool, thus counteracting the effects of any accidental mechanical distortion. The following four tables summarize the results obtained. All results are given in ohm-cm. $\times 10^9$.

Figure 1 shows the test circuit; instruments and wiring of the test-circuit were mounted on a polystyrene base 1 inch thick and dust free.

Examination of the foregoing tables prompts the following observations:

Remilling leads to distinctly higher resistivity.

Heat treatment leads to better batch-to-batch and within-batch correlation and tends to lower resistivity.

Vulcanizate variation between and within batches is great.

It can be concluded that large differences of electrical resistivity can occur in circumstances connected with the normal rubber-processing operations. These differences can be substantially reduced by extremely close control of mixing time and by careful handling and treatment of the vulcanizates, but the residual errors after all precautions are taken are still great.

II. COMPARISON OF TEST PROCEDURES AND ESTIMATION OF EXPERIMENTAL ERROR

In this work ten batches, each of the formula used in Part I were mixed, with a masterbatching system employed for all ingredients except carbon black and pine tar.

TABLE IV

Mold cavity no.	Batch			
	A	B	C	D
1	15	20	10	20
2	35	20	15	20
3	20	15	10	15
4	20	15	10	15
5	15	15	10	15
6	10	15	15	15
7	30	25	20	35
8	25	20	25	25
9	25	25	15	20

(Remilled. Heat-treated.)

		Cavities									
		a	b	c	d	e	f	g	h	i	k
Loadings	1.	E	B	F	D	G	J	A	C	H	K
	2.	K	G	A	J	B	D	F	H	C	E
	3.	C	K	D	B	E	G	J	A	F	H
	4.	D	A	E	C	F	H	K	B	G	J
	5.	B	J	C	A	D	F	H	K	E	G
	6.	F	C	G	E	H	K	B	D	J	A
	7.	J	F	K	H	A	C	E	G	B	D
	8.	G	D	H	F	J	A	C	E	K	B
	9.	H	E	J	G	K	B	D	F	A	C
	10.	A	H	B	K	C	E	G	J	D	F
	11.	C	K	D	B	E	G	J	A	F	H
	12.	G	D	H	F	J	A	C	E	K	B

Fig. 2.

One day after mixing, all batches were remilled for five minutes and sheeted out as nearly as possible to the same thickness, i.e., 0.02 inch thicker than the mold. After resting for 24 hours in a temperature and humidity controlled atmosphere (21° C; 60 per cent relative humidity), curing was carried out in the mold described in Part 1. A cure of 40 minutes at 138° C was used, and a die was employed for removing vulcanizates from the mold with minimum distortion. The samples of each batch were lettered according to the 12 × 12 Latin Square shown as Figure 2 and taken from Fisher's and Yates' standard tables (two columns omitted).

The day after curing, all specimens were cleaned with an acetone-moistened cloth and heat-treated for 1 hour at 100° C.

The day following heat treatment, all specimens were tested by the method described in Part 1 of this work and also by means of a null voltage circuit, which allowed resistivities of four 1-cm. portions of each test-piece to be measured². This null-voltage absolute method is, of course, free from contact resistance effects.

After testing, the brass-bonded electrodes were torn off and the bonds graded into categories G (good), M (medium), P (poor), B (bad). The whole experimental results are given in the following tables.

MIXING A
RESISTIVITIES IN UNITS OF 10³ OHM-CM.

Loading of mold	Position in mold	Absolute method					Method using brass-bonded electrodes	Ratio of results by two methods	Grading of bonds
		1	2	3	4	Average			
1	g	3.6	10.2	16.2	1.9	8.0	9.7	1.21	G.G.
2	d	7.5	11.5	9.5	8.2	9.2	8.0	0.87	M.G.
3	h	8.5	19.4	11.5	3.4	10.7	10.2	0.95	G.M.
4	—	—	—	—	—	—	—	—	—
5	d	6.9	8.4	10.7	11.1	9.3	9.0	0.97	G.G.
6	k	16.2	20.2	5.9	4.1	11.6	8.5	0.73	G.B.
7	e	6.5	8.8	7.4	3.9	6.7	7.3	1.09	G.G.
8	f	2.6	6.0	5.8	3.3	4.4	6.8	1.55	P.G.
9	j	2.3	3.0	21.2	5.4	8.0	8.0	1.00	P.M.
10	a	2.6	4.6	13.9	9.2	7.6	7.1	0.94	P.P.
11	h	7.2	19.8	2.8	1.3	7.8	7.1	0.91	G.G.
12	f	2.3	3.3	5.6	20.0	7.8	9.0	1.15	G.G.
13	h	6.3	9.8	16.7	6.6	9.9	10.9	1.10	G.M.

MIXING B
RESISTIVITIES IN UNITS OF 10^3 OHM-CM.

Loading of mold	Position in mold	Absolute method				Average	Method using brass-bonded electrodes	Ratio of results by two methods	Grading of bonds
		1	2	3	4				
1	b	6.8	9.6	13.4	11.7	10.4	9.5	0.92	G.G.
2	e	9.5	10.1	9.9	7.6	9.3	10.9	1.17	G.G.
3	d	2.4	4.1	16.1	7.0	7.4	8.7	1.18	G.P.
4	h	15.0	43.0	10.2	3.6	17.9	17.2	0.96	G.P.
5	a	1.3	2.5	25.8	6.3	9.0	9.0	1.00	P.G.
6	g	2.8	5.8	18.1	8.7	8.2	10.9	1.25	B.G.
7	j	4.6	13.0	75.0	1.4	23.5	20.4	0.87	M.G.
8	k	5.2	7.8	26.2	11.4	12.6	10.9	0.86	G.G.
9	f	4.5	10.7	29.9	23.7	17.2	10.2	0.59	G.M.
10	c	6.4	6.8	2.8	5.5	5.4	9.4	1.74	G.M.
11	d	16.0	23.3	9.3	4.4	13.2	12.3	0.93	G.G.
12	k	2.7	5.9	41.5	31.9	20.5	12.5	0.61	G.G.
13	-	-	-	-	-	-	-	-	-

MIXING C
RESISTIVITIES IN UNITS OF 10^3 OHM-CM.

Loading of mold	Position in mold	Absolute method				Average	Method using brass-bonded electrodes	Ratio of results by two methods	Grading of bonds
		1	2	3	4				
1	h	4.0	6.3	12.1	4.4	6.7	7.1	1.06	G.G.
2	j	4.0	8.6	17.6	4.9	8.8	9.5	1.08	G.M.
3	a	1.1	1.8	19.0	6.2	7.0	6.6	0.94	B.G.
4	d	20.8	9.5	8.7	6.1	11.3	8.3	0.74	G.G.
5	c	7.9	16.7	7.1	6.0	9.4	7.1	0.76	G.M.
6	b	3.0	4.5	6.8	4.3	4.7	4.7	1.00	G.B.
7	f	7.5	8.0	3.1	2.1	5.2	9.0	1.73	G.G.
8	g	20.3	9.7	1.7	1.4	8.3	5.7	0.69	G.G.
9	k	1.3	1.6	7.0	21.5	7.9	6.9	0.87	M.G.
10	e	12.9	7.3	5.0	4.1	7.3	6.6	0.90	G.G.
11	a	7.9	11.4	3.4	1.3	6.0	6.6	1.10	G.G.
12	g	4.0	3.0	21.0	1.1	7.3	6.9	0.94	M.P.
13	-	-	-	-	-	-	-	-	-

MIXING D
RESISTIVITIES IN UNITS OF 10^3 OHM-CM.

Loading of mold	Position in mold	Absolute method				Average	Method using brass-bonded electrodes	Ratio of results by two methods	Grading of bonds
		1	2	3	4				
1	d	8.3	13.3	5.6	3.2	7.6	6.6	0.87	M.M.
2	f	7.1	5.0	4.8	5.1	5.5	7.3	1.33	G.G.
3	c	5.0	8.3	23.0	11.8	12.0	9.2	0.77	P.P.
4	-	-	-	-	-	-	-	-	-
5	e	7.8	9.9	9.1	4.7	7.9	7.6	0.96	G.G.
6	h	4.7	15.3	7.3	2.8	7.5	7.6	1.01	P.G.
7	k	1.0	1.9	8.0	4.0	3.7	10.2	2.76	G.G.
8	b	4.7	6.5	12.3	4.2	6.9	6.4	0.93	M.G.
9	g	1.7	2.4	9.1	9.7	5.7	6.6	1.16	M.M.
10	j	16.9	2.9	1.3	1.1	5.6	5.9	1.05	G.G.
11	c	5.0	7.8	6.2	3.7	5.7	5.9	1.03	M.G.
12	b	3.5	12.2	4.7	2.5	5.7	7.3	1.28	G.M.
13	a	17.1	26.8	4.1	1.4	12.4	9.0	0.73	G.G.

MIXING E
RESISTIVITIES IN UNITS OF 10^3 OHM-CM.

Loading of mold	Position in mold	Absolute method				Method using brass-bonded electrodes	Ratio of results by two methods	Grading of bonds
		1	2	3	4	Average		
1	a	8.3	13.3	5.6	3.2	7.6	6.6	M.M.
2	k	4.1	2.1	9.1	28.0	10.8	7.8	G.G.
3	e	6.2	11.4	13.0	7.8	9.6	7.3	M.B.
4	c	6.9	9.2	19.0	9.8	11.2	9.2	G.G.
5	j	1.1	2.7	31.0	2.7	9.4	9.7	G.G.
6	d	10.6	13.5	9.8	3.5	9.4	6.8	G.M.
7	g	22.2	13.6	1.9	1.3	9.8	6.6	G.M.
8	h	5.8	15.8	18.4	4.0	11.0	11.1	G.G.
9	b	3.3	5.0	15.8	0.76	6.2	6.4	G.G.
10	f	7.2	10.5	16.7	9.3	10.9	8.3	M.M.
11	e	4.3	6.3	7.3	5.5	5.8	6.1	G.G.
12	h	6.7	17.5	5.9	3.1	8.3	7.8	G.G.
13	-	—	—	—	—	—	—	—

MIXING F
RESISTIVITIES IN UNITS OF 10^3 OHM-CM.

Loading of mold	Position in mold	Absolute method				Method using brass-bonded electrodes	Ratio of results by two methods	Grading of bonds
		1	2	3	4	Average		
1	c	6.1	8.5	9.2	8.6	8.1	7.3	G.G.
2	g	1.9	2.3	41.0	18.0	15.8	10.9	G.M.
3	j	4.2	5.6	18.3	6.4	8.6	11.1	G.P.
4	e	6.9	9.5	8.8	6.5	7.9	9.2	B.M.
5	f	7.8	8.7	8.0	7.2	7.9	14.4	P.M.
6	a	3.6	6.1	25.0	24.0	14.7	10.6	M.P.
7	b	11.6	15.3	3.8	2.3	8.3	8.5	G.G.
8	d	16.0	21.0	11.6	9.5	14.5	13.7	G.M.
9	h	5.9	10.3	9.6	6.0	7.9	8.5	M.M.
10	k	0.12	0.17	5.2	80.0	21.3	21.5	G.G.
11	j	7.1	23.8	15.8	8.2	13.7	11.1	G.G.
12	d	42.9	17.8	7.1	3.9	17.9	13.7	M.G.
13	-	—	—	—	—	—	—	—

MIXING G
RESISTIVITIES IN UNITS OF 10^3 OHM-CM.

Loading of mold	Position in mold	Absolute method				Method using brass-bonded electrodes	Ratio of results by two methods	Grading of bonds
		1	2	3	4	Average		
1	e	13.2	6.2	5.8	2.0	6.8	5.2	G.G.
2	b	7.8	16.6	5.0	3.6	8.2	7.1	G.G.
3	-	—	—	—	—	—	—	—
4	j	4.8	27.2	4.9	2.9	9.9	8.0	P.P.
5	k	11.6	1.8	4.9	12.1	5.1	5.2	G.P.
6	c	13.4	9.9	9.6	7.8	10.2	7.3	G.M.
7	h	3.6	6.6	17.6	7.1	8.7	6.8	M.G.
8	a	8.8	8.5	3.7	1.1	5.5	5.7	G.G.
9	d	3.7	6.6	1.2	0.9	3.1	7.1	G.M.
10	g	1.9	3.7	13.0	5.9	6.1	5.9	M.G.
11	f	5.3	12.2	9.2	2.9	7.4	7.3	G.G.
12	a	11.8	11.8	3.7	1.9	7.3	5.2	G.G.
13	f	4.5	5.2	22.0	11.5	10.8	8.3	G.M.

MIXING H
RESISTIVITIES IN UNITS OF 10^3 OHM-CM.

Loading of mold	Position in mold	Absolute method					Method using brass-bonded electrodes	Ratio of results by two methods	Grading of bonds
		1	2	3	4	Average			
1	j	9.6	16.7	6.2	2.9	8.9	8.7	0.98	G.G.
2	h	5.2	7.0	13.2	4.6	7.5	9.4	1.25	G.G.
3	k	5.1	7.0	15.0	7.3	8.6	9.9	1.15	M.P.
4	f	7.2	20.1	2.2	1.8	7.8	8.0	1.03	P.G.
5	g	2.3	2.9	27.6	10.4	10.8	9.9	0.92	B.P.
6	e	6.7	5.0	10.1	5.7	6.9	7.3	1.06	G.P.
7	d	8.6	9.2	16.6	7.4	10.5	9.0	0.86	M.G.
8	c	8.0	13.5	15.3	11.7	12.1	9.9	0.82	G.G.
9	a	2.0	2.7	28.3	14.7	11.9	9.2	0.77	G.G.
10	b	7.0	15.7	8.6	3.8	8.8	8.3	0.94	M.M.
11	k	9.6	31.0	2.0	1.1	10.9	9.2	0.84	G.G.
12	c	6.3	11.2	17.3	9.2	11.0	9.0	0.82	P.B.
13	-	—	—	—	—	—	—	—	—

MIXING J
RESISTIVITIES IN UNITS OF 10^3 OHM-CM.

Loading of mold	Position in mold	Absolute method					Method using brass-bonded electrodes	Ratio of results by two methods	Grading of bonds
		1	2	3	4	Average			
1	f	29.6	13.1	2.3	1.5	11.6	7.8	0.67	G.G.
2	d	3.5	4.4	15.4	12.7	9.0	7.6	0.84	G.G.
3	g	15.1	13.0	2.7	1.9	8.2	5.9	0.72	P.M.
4	k	0.9	1.4	19.4	17.6	9.8	7.8	0.80	G.G.
5	b	4.6	8.9	11.7	4.4	7.4	7.3	0.99	B.P.
6	j	1.8	3.9	27.5	4.9	9.5	8.3	0.87	P.G.
7	a	5.1	14.1	2.8	1.1	5.8	6.9	1.19	P.G.
8	e	6.5	9.9	6.5	4.0	6.7	5.7	0.85	G.M.
9	c	8.6	4.6	7.1	6.2	6.6	6.6	1.00	M.G.
10	h	4.3	7.8	17.5	10.6	10.0	7.8	0.78	G.M.
11	g	8.2	11.2	1.3	0.8	5.4	6.9	1.28	G.G.
12	e	30.0	7.3	3.2	1.7	10.5	9.5	0.90	M.G.
13	-	—	—	—	—	—	—	—	—

MIXING K
RESISTIVITIES IN UNITS OF 10^3 OHM-CM.

Loading of mold	Position in mold	Absolute method					Method using brass-bonded electrodes	Ratio of results by two methods	Grading of bonds
		1	2	3	4	Average			
1	k	23.4	18.0	4.1	2.0	11.9	8.5	0.71	G.G.
2	a	3.7	3.7	12.9	10.9	7.8	6.6	0.85	M.G.
3	b	0.64	56.0	2.2	1.8	15.2	10.9	0.72	P.B.
4	g	1.9	2.1	49.3	10.0	15.8	10.9	0.69	P.B.
5	h	4.8	27.1	8.1	2.8	10.7	8.0	0.75	M.M.
6	f	13.3	19.0	7.9	4.9	11.3	8.0	0.71	G.M.
7	c	4.2	13.8	8.8	6.2	8.2	8.0	0.98	M.G.
8	j	7.1	17.6	5.1	1.1	7.7	7.6	0.99	G.P.
9	e	3.7	10.7	5.8	4.0	6.1	7.3	1.20	G.P.
10	d	2.0	2.4	7.0	21.0	8.1	8.3	1.03	G.M.
11	b	3.2	8.8	7.3	4.7	6.0	6.4	1.07	G.G.
12	j	5.8	18.1	16.0	3.9	10.9	9.0	0.83	G.G.
13	-	—	—	—	—	—	—	—	—

Analyses of variance were made on:

- The logarithms of values by the brass-bonded method.
- The logarithms of the arithmetic means of the four results by the absolute method.
- The logarithms of the ratios:

$$\frac{\text{resistivity by brass-bonded method}}{\text{resistivity by absolute method}}$$

These analyses lead to the following conclusions.

- Neither method shows a significant effect due to cavities or loadings, but despite this fact it is advisable to use latin square curing design for further work.
- Lumping the sums of squares due to cavities and loadings with the residual, the following mean squares and degrees of freedom are found.

	Degrees of freedom	Brass- bond	Mean squares absolute	Components of variance
Between mixings	9	0.064	0.052	$10 S_m^2 + S_o^2$ S_o^2
Within mixings (residual)	90	0.0078	0.0187	

S_o^2 is residual variance; S_m^2 the between-mixing variance. The variance ratio test shows that the between-mixing mean squares, which in themselves are highly significant, are not significantly different for the two methods.

- The arithmetic mean values of the ratio for the samples marked "Bad" is 0.91.

A number of other interesting statistical conclusions can be drawn, but for all practical purposes it is sufficient to say that the simpler brass-bonding technique is free from contact-resistance errors, and the strength of bond is of no importance within the range of bonds found in this work.

III. EFFECT OF FLEXING ON RESISTIVITY

Four batches of the following composition were mixed, and two brass-bonded specimens from each, vulcanized 40 minutes at 138° C, were prepared, using the mold and technique described earlier in this report.

Smoked sheet rubber	100
Stearic acid	2.5
Zinc oxide	5
C.B.S.	0.5
Sulfur	2.5
Pine tar	4.5
HAF black	50

Each of these specimens was mounted in turn in the Goodrich flexometer in the manner shown in Figure 3. The whole electrical circuit was insulated by means of polystyrene.

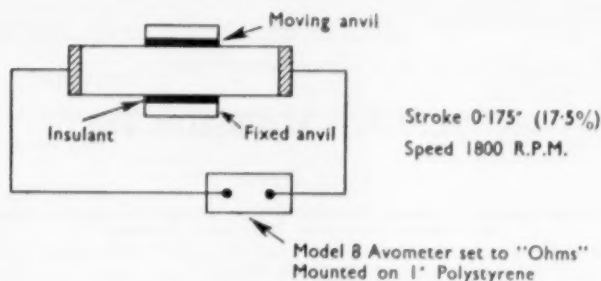


FIG. 3.

Resistances calculated in ohms $\times 10^3$ under various conditions are recorded in the table below.

Batch	Specimen	Initial stationary	Time running (seconds)			Time stationary after running (seconds)		
			5	30	60	5	30	60
A	a	30	5000	5000	4000	500	180	150
	b	30	5000	5000	4000	500	220	190
B	a	32	5000	5000	2800	300	120	100
	b	26	7500	7500	7500	2000	220	170
C	a	33	4500	3000	3000	400	200	100
	b	26	4000	2600	2500	400	180	150
D	a	29	2500	4000	4500	350	200	175
	b	23	2500	4500	4500	300	110	110

The results of this experiment show that a profound and immediate increase of resistivity takes place at the commencement of flexing and that a large decrease of resistivity takes place as soon as flexing ceases, followed by further slower decrease.

SUMMARY

Considerable differences may exist between volume resistivities of vulcanizates prepared from a single mixing. Large differences between mixing effects can also occur.

Contact resistance effects caused by bonded brass electrodes are shown to be negligible over a considerable range of bond strengths.

The profound effects of compressive flexing on the resistance of vulcanizates is demonstrated.

A formula containing sufficient HAF black to place the vulcanizates nominally in the electrically antistatic range was employed throughout the work.

ACKNOWLEDGMENTS

The author's thanks are due to R. H. Norman and H. A. Curran for valuable assistance and comment, and to the Directors of R. W. Greeff & Co., Ltd., for permission to publish this paper.

REFERENCES

- ¹ In accordance with draft specification CM(RUC)72 (since published as B.S. 2044/53).
- ² Norman, *Trans. Inst. Rubber Ind.* 27, 276 (1951).

PULL-THROUGH ADHESION TEST *

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INTRODUCTION

The adhesion of tire cord to a rubber compound is now usually characterized by quoting the force required to extract the cord from a test block of that compound. In a standardized form, the H-test, as it is sometimes called, is described in a paper by Lyons and coworkers, who describe a further detailed study of the more important factors operative while the specimen is under preparation, and during the test itself.

The present paper is devoted to an extended study of a modified form of the H-test; in particular, how the pull-through force is influenced by cord tension during cure, rate of loading during test, diameter of specimen mount, twist in the cord, temperature of test, and cord length embedded in the rubber, together with some theoretical considerations of the mechanics of adhesion breakdown.

DESCRIPTION OF TEST

The cords to be tested are mounted on a frame under a tension of 100 gm. $\frac{1}{4}$ -inch apart and 48 in number; they form an unwoven ply in the middle of a $\frac{3}{8}$ -inch deep cavity (Figure 1). On either side of the ply is placed a $\frac{3}{8}$ -inch

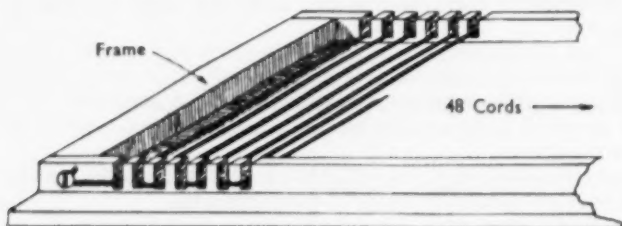
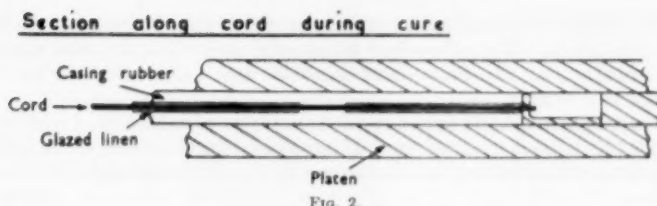


FIG. 1.

layer of rubber compound from which the cord is insulated by glazed Holland fabric, except in the test block region, where slots $\frac{1}{8}$ -inch wide are cut on each layer (Figure 2). The protecting $\frac{1}{8}$ -inch wide fabric is removed at the latest convenient stage during construction, thus reducing contamination of the rubber surface to a minimum. The frame is then placed within a simple rectangular mold and cured in a steam-heated daylight press at a mean pressure of 200 lb. per sq. in. of rubber surface area and 300° F for 35 minutes.

After cure, the resultant rubber slab consists of a strip $\frac{1}{8}$ inch thick through which the cords pass and to which they are bonded. On either side the cords pass into a pocket formed on the inside by the glazed Holland and outside by

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the $\frac{3}{16}$ -inch layers of rubber. It has been found most convenient to remove these by cutting them away with a pair of sharp nail scissors. There then remains only the $\frac{3}{8}$ -inch square section of rubber with cords protruding on either side. The cords on one side are cut away, leaving the specimen ready for test.

This is performed on an inclined-plane tensile tester (Scott I.P.4). The specimen is mounted against a slotted plate, with the cord passing through the slot, and gripped in the jaw of the test machine (Figure 3). The machine is set in motion, and the pull-through force is recorded on the chart exactly as in normal tensile tests on tire cords.

INTRINSIC VARIATIONS OF THE ADHESIVE FORCES

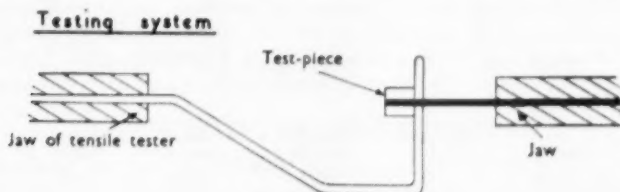
Tests within the same specimen.—Some variation between any pull-through tests on supposedly identical specimens is expected as a matter of course; however much care is taken to keep cord and rubber conditions the same throughout the specimen. It may be more marked when the cords selected for comparison are wider apart. It was the subject of an experiment in which all the 48 low-stretch cotton cords (3/4/16.7's) were extracted from one test-piece and the adhesion values studied in groups of eight.

Cord numbers	1-8	9-16	17-24	25-32	33-40	41-48	Grand mean
Group mean (pull-through in lb.)	6.4	6.2	5.9	6.1	6.4	6.3	6.2
Group variance (lb. ²)	0.060	0.070	0.054	0.050	0.103	0.130	0.078

Analysis of variance

Source of variance	Degrees of freedom	Sum of squares	Mean squares	Variance ratio F	P
Between groups	5	1.52	0.304	$\frac{0.304}{0.078} = 4$	0.01
Within groups	42	3.27	0.078		
Total	47	4.79			

Thus, the statistical treatment shows the variation between the groups to be significantly greater than the variation within the groups; a result which confirms our expectations. Nevertheless the variation across the whole specimen is



very small when compared with the differences between different types of cord or cord treatment. Thus the effect of between-cord variation need not hinder experimental work. An example of a routine test between cotton and rayon illustrates this feature.

A test was arranged to compare the same type of cotton cord with a rayon cord (3/1180 denier) treated with a latex-resorcinol-formaldehyde adhesive. The cords were studied in groups as shown in the following table.

Cord type	Cotton		Rayon	
Position in ply	1-12	25-36	13-24	37-48
Group mean (pull-through in lb.)	9.1	9.2	7.6	7.4
Group variance (lb. ²)	0.24	0.20	1.02	1.32
Mean for cord type (lb.)	9.15		7.5	
Variance for cord type (lb. ²)	0.22		1.18	

Analysis of variance

Source of variance	Degrees of freedom	Sum of squares	Mean squares	Variance ratio F	P
Between cotton and rayon	1	34.7	34.7	34.7/0.68 = 51	<0.001
Between groups of same cord	2	0.30	0.15	0.7 = 5	N.S.
Within groups	44	30.8	0.7		
Total	47	65.8			
Between groups + within groups	46	31.1	0.68		

In contrast to the results on cotton cords alone, the variation between groups of the same type of cord, i.e., cotton or rayon, is not greater than that expected from the estimated variation between individual cords; the fact that the within-group mean square is greater than that between groups of the same cord is unexpected, but is apparently due to sampling errors. The difference between the adhesion values for cotton and rayon is very large; a chance difference as large as this could occur only once in more than a thousand times.

Variations between specimens.—When tests are made on several cord-rubber slabs, constructed from nominally identical cord and rubber compound, it is found that the variation of pull-through force between the slabs greatly exceeds that within the slabs. An impression of this variability is provided by the following figures.

Number of observations	Average pull-through (lb.)	Variance
24	9.1	0.22
48	8.2	0.13
8	11.0	0.41
8	10.7	0.49
16	8.4	0.12
8	7.5	0.09
16	8.8	0.28
8	8.1	0.07
6	8.4	0.13
6	9.1	0.17
Total 148	Grand mean 8.8	

Analysis of variance

Source of variance	Degrees of freedom	Sum of squares	Mean squares	Variance ratio F	P
Between specimens	9	95.4	10.6	56	<0.001
Within specimens	138	26.09	0.19		
Total	147	121.49			

The statistical treatment confirms the greater degree of variability between specimens, which is understandable when account is taken of all the variables introduced between slabs. It is thus essential to make all comparisons between cords or other variables within the same test-specimen.

Interaction between adjacent cords.—Only $\frac{1}{4}$ -inch separates the cords in the test block. It is reasonable to suspect that performing a pull-through test on one cord will affect its neighbor. Apart from the deterioration of the bond itself, the existence of a hole, formerly occupied by a cord, may alter the mechanism of the pull-through process to an appreciable extent.

To assess the interaction experimentally, a test was made on 48 cotton cords in one test-specimen. The first 16 were pulled out in order from 1 to 16. Next the remaining even cords were extracted, and finally the odd-numbered cords were pulled through.

It might be expected that the even-numbered cords, with a protecting cord on either side, would be least affected by previous distortion. Next should come numbers 1 to 16, and finally the odd-numbered cords. However, the results obtained were not in that order.

Cord numbers	1-16	Even 18-48	Odd 17-47
Pull-through (average in lb.)	8.82	8.74	8.48
Variance	0.28	0.12	0.29

Analysis of variance

Source of variance	Degrees of freedom	Sums of squares	Mean squares	Variance ratio F	P
Between groups	2	1.01	0.51	2.1	>0.05
Within groups	45	11.04	0.24		
Total	47	12.05			

It may be concluded that the interaction effect, if it exists, is very small.

It should be noted that, during all routine tests, the cords are pulled out in order from 1 to 48 across the block. Any effect of the type sought here would, therefore, tend to operate as a constant added to the pull-through values obtained. Comparisons in the same block would thus still remain valid.

AGING TEST

Since it is of interest to know the effect of storage on the pull-through force, a series of tests was carried out. The values found at intervals of time up to 9 days after completion of cure are quoted in the following table.

Number of cords	1-8	9-16	17-24	25-32	33-40	41-48
Time of storage (minutes)	53	160	480	1,440	4,320	12,960
Average pull-through (lb.)	8.6	8.25	8.3	8.1	8.3	8.7
Variance	0.13	0.26	0.10	0.07	0.30	0.18

A regression analysis confirms the general impression that there is little or no change in pull-through value. However, this does not prove that a change will not occur when different cords, adhesives, and rubber compounds are involved, and therefore aging effects should always be guarded against.

THE EFFECT OF CORD TENSION

When a routine test is to be made, the cords are mounted on the frame at a standard tension of 100 grams. It is conceivable that a variation of this tension may produce an additional component of variation of the final pull-through

figure; at higher tensions the highly twisted cord becomes compressed, thereby presenting a smaller surface area to the rubber and also inhibiting rubber penetration into the cord; on this basis an increase in tension should reduce the pull-through figure, most probably according to a logarithmic law, such a relation being a common feature in theoretical treatments of yarn and cord structure. To test this proposition, a series of tensions was applied to the cord during test-piece construction. The average values for the various tensions may be seen from the graph (Figure 4).

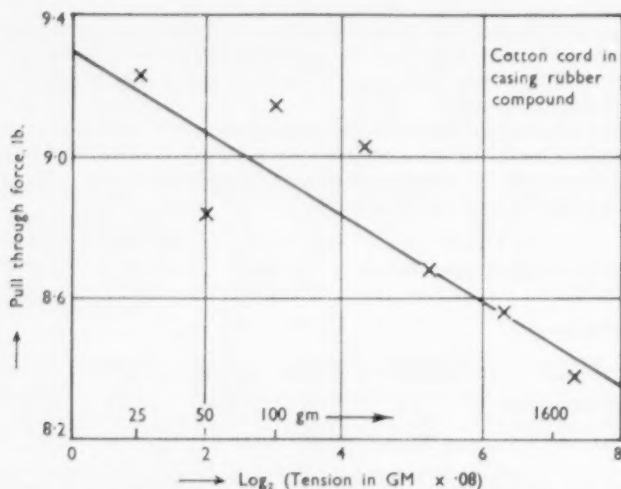


FIG. 4.—The effect of cord tension during mounting on the pull-through force.

Statistical analysis showed a significant regression of pull-through load on a logarithmic function of the tension ($P < 0.001$). The best linear function expressing this relationship was found to be:

$$y = 9.32 - 0.116x$$

where $x = \log_2 \frac{(\text{tension of cord in g.})}{12.5}$

The relationship may be summarized most simply by stating that, if the standard tension of 100 grams is either halved or doubled, the pull-through value will be changed by only ± 1.3 per cent; thus tension during construction can hardly be regarded as a very critical factor in producing variability of the final test figure.

THE EFFECT OF RATE OF LOADING

The strength of most viscoelastic structures is susceptible to the rate of loading, or to the rate of applied extension. The test-piece is no exception to this rule; the effect is found to be marked over the wide range made possible by controlling the operating speed of the inclined plane tensile testing machine.

Eight rates of loading were chosen, and these were randomly distributed within six successive groups across the specimen. The cotton cord was the same as that used in previous investigations.

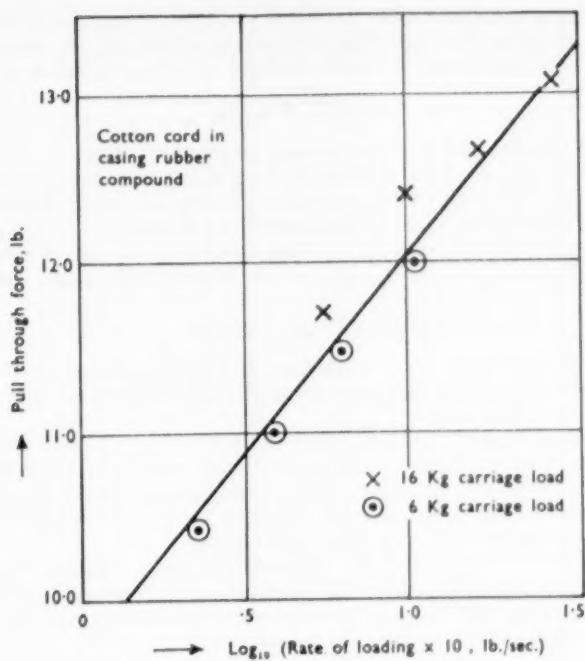


FIG. 5.—The effect of rate of loading on the pull-through force.

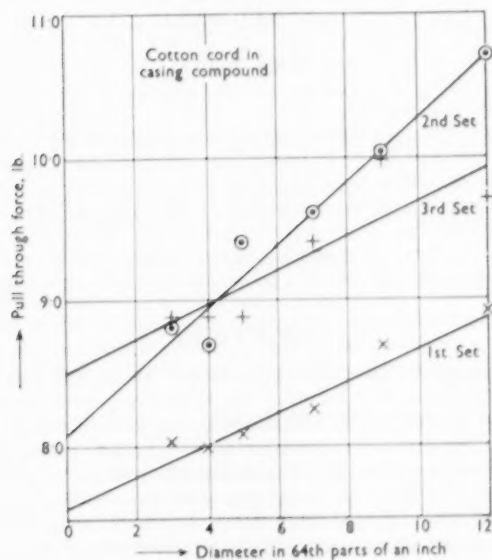


FIG. 6.—Pull-through force vs. mounting diameter.

By carrying out a statistical analysis, a significant regression of the pull-through load (y) on the logarithm of the rate of loading (x) was found ($P < 0.001$). The best linear function relating y and x was found to be

$$y = 9.7 + 2.44x$$

In Figure 5 this line and the experimental points are plotted.

The satisfactory fit of the data to the logarithmic form brings it into agreement with the other textile findings, where it is now well established that break and rate of loading are related by a logarithmic function². In the particular instance just considered, we may say that a two-fold increase of the standard speed of testing has produced roughly a 7 per cent increase of the pull-through force.

THE MOUNTING DEVICE

Several possible methods of mounting have been suggested; they include a clamp or vice system, in which the rubber specimen is bonded to the mounting plates, and the simple slot.

The method chosen may well affect the pull-through force. To test this without undue complication, no great departure was made from the simple slotted plate technique; six holes of increasing diameter were drilled in a steel strip and this was placed between the specimen and the slotted plate; in effect the slot was replaced by one or other of the holes.

Three separate tests were made, using a cotton cord. Each showed that the pull-through force increased with the diameter. If y denotes the pull-through force in lb., and x is the diameter in sixty-fourth parts of an inch, the best line relationships were found to have the equations:

$$y = 7.6 + 0.11x$$

$$y = 8.1 + 0.22x$$

and

$$y = 8.5 + 0.12x$$

They are plotted in Figure 6.

The statistical analysis also showed that the regression of y on x was significant at the 1 per cent level for the first line, whereas the second and third were significant at the 0.1 per cent level.

In round figures it may be stated that a $1\frac{1}{2}$ to $2\frac{1}{2}$ per cent change in pull-through force results from a change of $1/64$ inch in diameter.

The effect is small but appreciable, and we may, therefore, conclude that a larger change might be expected if a gross change in the mounting system were made.

CABLE TWIST

Previous work on cotton cord has shown a small though significant increase in the pull-through value with twist¹. The same process was therefore repeated on a rayon cord (2/1650 denier) within a twist range of $2\frac{1}{2}$ and 15 turns per inch.

The first experiments on rayon were made on a pretreated yarn, which required no adhesive treatment after the cord-making stage. In subsequent tests conventional methods were followed; the cord was made from standard 1650 denier yarn and then dipped in a latex-resorcinol-formaldehyde adhesive. Although the first experiments exhibited a relatively small degree of variability with a coefficient of variation of $4\frac{1}{2}$ per cent, the later tests reached the 10 to 11

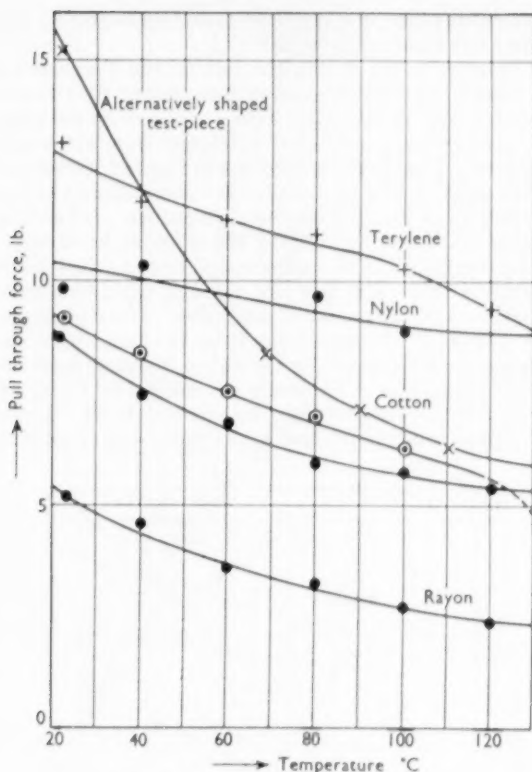


FIG. 7.—Pull-through force vs. test temperature.

per cent range. This demonstrates the high level of variability introduced by an adhesive dip applied to the cord rather than to the yarn.

In none of the tests was there any significant trend of pull-through force with the twist. It was concluded, therefore, that the effect, if it exists, must be small.

THE EFFECT OF TEMPERATURE

It is common knowledge to tire technologists that the cord-rubber bond tends to weaken as the temperature rises. Investigations have been made by Lyons and coworkers on cotton cord¹. In the present studies a variety of cords were tested over a range, starting at room temperature, and, in general, going up to 120° C.

Tests were performed in a hot box mounted on the inclined plane tensile tester. Care was taken to dry the specimens to eliminate moisture effects; a drop of some 25 per cent of pull-through force had been noted when a rayon pull-through specimen was wetted.

As may be seen from Figure 7 the downward trend persists over the whole temperature range, with a more rapid drop at lower temperatures. Provided the temperature does not exceed about 120° C, the effect is reversible. Beyond

this, degradation takes place; in a specimen tested up to 160° C, the linear plot (Figure 8) drops away rapidly above 120° C.

A particular feature noted during the test on the Terylene cord was the transfer of the breakdown from the cord surface (20° to 80° C) into the rubber surrounding the cord (80° to 120° C). This was shown by the irregular sheath of rubber which enclosed the cord after extraction from the test-piece at the higher temperatures. The curve for Terylene in Figure 7 includes a discontinuity around 80° C, also pointing to a change in the breakdown system.

The linear relations of Figure 8 require explanation. It has been suggested that the energy of activation for forming the adhesive bond may be assessed from a plot of the logarithm of the pull-through force against the reciprocal of the absolute temperature. The best line through the points should then be regarded as a measure of the energy of activation. Very satisfactory straight lines have been obtained. However, the slope is altered by a change of the test-piece dimensions, as instanced by the values obtained from the test-piece designed for another machine. Evidently one additional factor at least is involved besides the energy of activation of the adhesive bond. In the Appendix, the mechanism of the pull-through test is analyzed; it is apparent that a tem-

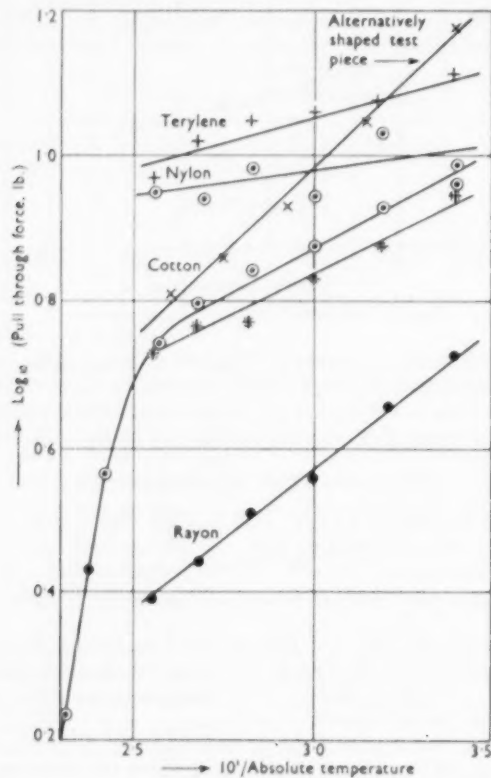


FIG. 8

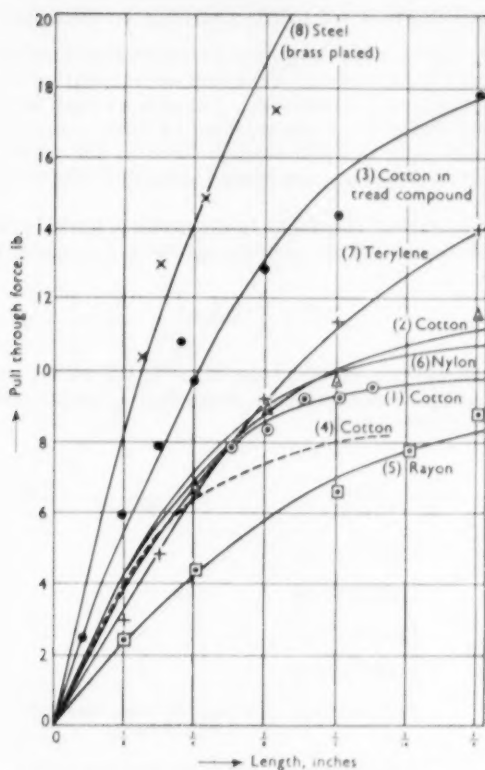


FIG. 9.—Pull-through force vs. cord length embedded in rubber.

perature dependence of cord or rubber modulus leads to a change of the pull-through figure with changing temperature, apart from the effect of temperature on the bond itself.

Further details of these linear plots are given in the following table:

x = reciprocal of the absolute temperature.

y = \log_{10} (pull-through force in lb.).

P = significance level.

Cord	Adhesive system	Regression line	$P(\%)$
Cotton 3/4/16.7's	Untreated	$y = 0.248x + 0.095$	<0.1
Cotton 3/4/16.7's	Untreated (different mold)	$y = 0.471x - 0.432$	<0.1
Cotton 3/4/16.7's	Untreated	$y = 0.264x + 0.082$	<0.1
Rayon 2/1650 denier	Dipped in latex-resorcinol-formaldehyde	$y = 0.348x - 0.582$	<0.1
Nylon 3/3/210 denier	Dipped in latex-resorcinol-formaldehyde	$y = 0.075x + 0.761$	<2.0
Terylene 3/5/140 denier	Dipped in latex-resorcinol-formaldehyde	$y = 0.140x + 0.635$	<0.1

THE EFFECT OF CORD LENGTH IN RUBBER

On increasing the bonded length, a proportionate increase of the pull-through force would be expected. To a first approximation this is true, provided only short lengths are considered. But as the length increases, the pull-through force drops below the value expected by direct proportion. The tests performed illustrate this; the pull-through force at the greater lengths falls away so much that the force appears to tend asymptotically to a constant value (Figure 9).

An idealized theoretical treatment of the problem leads to this same result (Appendix). It is found that the pull-through force T is related to the length l by the relation:

$$T = \frac{k}{n} \tanh nl$$

Hyperbolic tangent curves have been fitted to the points, and the limiting values at $l = 0$ have provided estimates of the shear force per unit area required to produce adhesion breakdown.

Cord	Rubber compound	Adhesive	Cord diam. (thou-sandths)	Shear force (lb. per sq. in.)
1. Cotton 3/4/16.7's (high stretch)	Typical casing	—	32	340
2. Cotton 3/4/16.7's (low stretch)	Typical casing	—	32	300
3. Cotton 3/4/16.7's (low stretch)	Typical tread	—	32	430
4. Cotton 2/211.6's (high stretch)	Typical casing	—	23	460
5. Rayon 2/1650 denier	Typical casing	Dipped in latex-resorcinol-formaldehyde	28	210
6. Nylon 3/3/210 denier	Typical casing	Dipped in latex-resorcinol-formaldehyde	20	500
7. Terylene 3/5/140 denier	Typical casing	Dipped in latex-resorcinol-formaldehyde	22	400
8. Steel	Typical casing		35	600

These figures are for particular samples of cord and dip and are not necessarily typical values; thus the figure for rayon is probably rather low, while those for nylon and Terylene are above average; all are laboratory-prepared specimens, with adhesive pick-up levels in excess of those usually obtained. The figures are quoted solely to demonstrate the information which may be obtained from a test on cord length against pull-through force.

The agreement between the test values and the hyperbolic tangent curves may be assessed from the plot of the theoretical value against the test values (Figure 10).

The theoretical approach is, of course, idealized and departs considerably from the real mechanics of the system, particularly at higher values. For example, the steel cord should give a straight line, but the curve is almost the same as that obtained for a similar textile cord of much lower modulus. Thus the remarkable feature of the tests as a whole is their closeness to the hyperbolic curve obtained theoretically, although the assumptions of the theory are so far

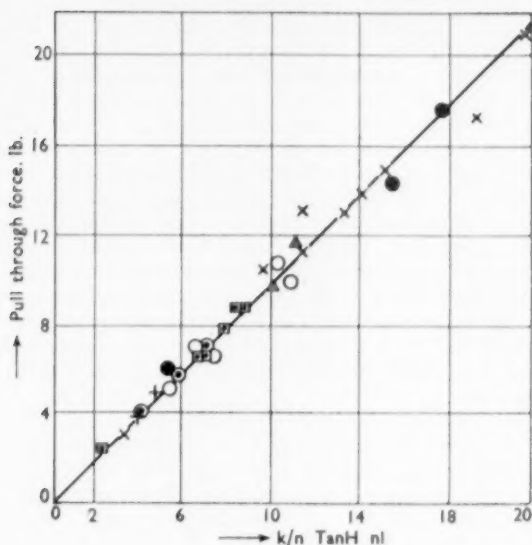


FIG. 10.

Cord	Symbol	K/n	n
1. Cotton	○	10	3.45
2. Cotton	△	11.7	2.6
3. Cotton	●	19	2.3
5. Rayon	□	9.2	2.01
6. Nylon	○	11	3.1
7. Terylene	+	17	1.65
8. Steel	×	45	2.6

removed from practice. Evidently a revised theoretical treatment should also yield a hyperbolic tangent relation or a closely related form. It is an interesting feature that an exponential function has usually been obtained when other bonded systems have been analyzed³.

THE RELEVANCE OF THE PULL-THROUGH TESTS TO PRODUCT PERFORMANCE

Here it becomes necessary to depart from the precise experimentation possible only in the laboratory, and turn to the very difficult problem of how the test may be related to the performance of a commercial cord-rubber structure. In attempting a general answer to the question, account must be taken of the great diversity of products, the varied conditions of their application, and the complicated structure of the product itself. It seems probable that an answer, based on quantitative performance figures which include all the factors mentioned, would require information on the subsequent history of an appreciable percentage of the total output of the product.

It is much easier, therefore, to try to make an assessment of the forces acting in the product, and to compare them with the forces which apply throughout the test. The remarks that follow apply to a tire, though it is possible that the same considerations might apply to other structures.

It is maintained that adhesion failure in a tire is largely caused by the shear forces transmitted across the cord-rubber interface.

So far there is fair agreement on the mechanism, but now a critical point is reached; failure in the tire is not usually immediate, but is apparently the result of successive shear loads applied at the interface, of a magnitude less than the critical shear stress reached in the operation of the pull-through test. If this were not so, and the critical value were reached as soon as the tire was put into service, breakdown of the bond would follow instantly, and subsequent performance might well be limited to a matter of minutes before the breakdown of the tire itself. Such failures have, indeed, been quoted in exceptional cases.

On this argument, there is evidently considerable use for the pull-through test in a sorting capacity; with its aid it should be possible to detect several cord-adhesive-rubber systems which will fail at a very early mileage. It does not follow that all will be eliminated by this test; nor is the dividing line clear between those that will fail outright and those that will provide a reasonable performance.

At higher levels of adhesion it appears that resistance to fatigue, as well as intrinsic bond strength, enters the argument. If fatigue is defined as the rate at which the bond strength decays, it becomes possible to postulate a second class of bonds with a poor performance: namely, those whose static test figures may be moderate or even good, but whose fatigue resistance is very poor; such bonds will not be eliminated by the test. Similar considerations appear to apply equally well to any other type of static test where dynamic performance is required of the finished product.

As a special case it is worth considering the conditions where the rate of fatigue depends on the magnitude and frequency of the dynamic stresses applied, and not on the system of bonding used. The time for the bond strength to fall to the critical level at which the composite product falls apart will then depend on the stress history and the initial level of adhesion. A higher initial level of adhesion cannot do other than yield a product having a longer life; the corollary to this is that a static test would provide all the information required.

However, since this special case is unlikely, and since it would require proof by the use of a dynamic test, it may be concluded that the pull-through test can only be expected to act in a preliminary sorting capacity. When a more accurate assessment of the potentialities of a bonding system is required, dynamic adhesion tests must be used.

SUMMARY

A modified form of the pull-through test is described, followed by a series of experiments, the first three of which demonstrate the precision of the method. Further experiments assess the effect of various factors on the pull-through force. It is found that specimen age has little effect. The tension applied to the cord during construction also produces a small but appreciable effect, amounting to a decrease of 1.3 per cent for a two-fold increase of the tension, but a greater effect, amounting to a 7 per cent increase of the pull-through force, is obtained when the rate of loading is doubled. The pull-through force is also shown to depend on the shape of the mounting device. The twist in a rayon cord does not give a significant effect, though the variability exhibited by the conventionally dipped cord is high. Temperature increase during test reduces the pull-through force; linear plots of the logarithm of the pull-through force against the reciprocal of the absolute temperature are obtained. The cord

length embedded in the rubber is shown to bear a hyperbolic relationship to the pull-through force, confirming the theoretical relationship obtained analytically. Finally the pull-through test is considered in terms of the product.

ACKNOWLEDGMENT

The author is indebted to his colleagues for their helpful criticism; in particular to J. W. Illingworth, under whose direction the work was carried out. Publication of the paper was made possible by the kind permission of the Directors of the Dunlop Rubber Company Ltd.

REFERENCES

- ¹ Lyons, Nelson, and Conrad, "Study of the H test for evaluating the adhesive properties of tire cord in natural and GR-S rubbers", Southern Regional Research Laboratory, U. S. Dept. of Agriculture, October 1945.
- ² Maisch, "Effect of speed of testing on rayon and cotton yarns, cords, and fibers", ASTM Bulletin No. 161, p. 27 (1949).
- ³ deBruyne and Houwink, "Adhesion and Adhesives", Elsevier, London, 1951, Chapter 4, Part 1.

APPENDIX

The force and deformation in the test-piece.—Since the relation between the pull-through force and the length of cord embedded in rubber appears to be non-linear, an analysis of the equilibrium of a small cord element is made here. Subsequent integration over the length embedded in rubber then enables us to determine the pull-through force as a function of the length. The analysis also takes into account certain geometric and elastic properties of the system.

If Young's modulus for the cord is E , and the force per unit area across a section of the cord is F , the state of strain may be found and related to the stress. Consider a displacement in which A moves to A' , a distance u while B moves to B' , a distance $u + \frac{du}{dx} \delta x$. The small element AB of length δx is strained to an extent $\frac{du}{dx}$. Whence

$$F = E \frac{du}{dx} \quad (1)$$

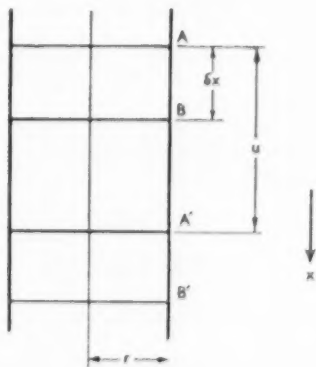


FIG. 11.

The equilibrium of the small element AB depends on the balance between the forces acting across the sections at A and B , respectively, and also on the shear force at the interface.

It is now necessary to postulate a relation between the shear force and the displacement. Some indication of the form of this relation may be obtained by considering a special case. A cylinder of rubber rigidly supported at its outer curved boundary has running through its center a rigid cord. If a load is applied to the cord, it is easy to show that the displacement is proportional to the load. Turning now to the test-piece used in our present work, it may be argued that the outer parts of the rubber block remain relatively rigid, supported by the slotted plate, while an inner cylindrical region corresponds in behavior to the cylinder of our special case. Thus we may with some justification assume a linear relation as an approximate representation of the conditions which obtain during the test. In algebraic terms we may now state:

$$f = cu \quad (2)$$

where f is the shear force per unit area of interface and c is a function of the geometry and the modulus of the rubber test-piece. On taking into account all the forces acting on the small element AB , it is found that the equilibrium condition reduces to:

$$\frac{dF}{dx} = \frac{2cu}{r} \quad (3)$$

We now possess all the information required to obtain general equations for stress, etc., in the specimen. Integrate Equation (1) with respect to x and equate the resultant expression for $\frac{dF}{dx}$ to the expression given by Equation (3).

$$\frac{d^2u}{dx^2} = n^2u \quad (4)$$

where

$$n^2 = 2c/Er \quad (5)$$

The general solution to the equation reads:

$$u = A \sinh nx + B \cosh nx \quad (6)$$

and

$$F = En(A \cosh nx + B \sinh x) \quad (7)$$

using the relation of Equation (1).

At the free end of the cord, where $x = 0$, the force drops to zero; thus on inspection of Equation (7) it is evident that the constant A is zero. The solution therefore becomes:

$$u = B \cosh nx \quad (6a)$$

and

$$F = EnB \sinh nx \quad (7a)$$

and it is found that

$$F = Enu \tanh nx \quad (8)$$

when B is eliminated from the two solutions.

The distribution of stress and displacement are illustrated in Figure 12.

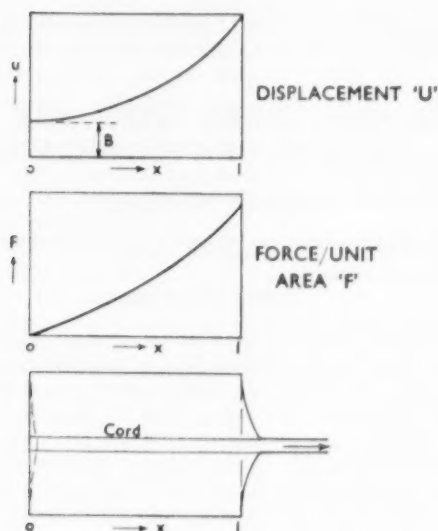


FIG. 12.

Since the shear stress is proportional to the displacement, it is evident that that the shear reaches a maximum at the point of emergence.

Breakdown will, therefore, occur first when the shear in the emergent region reaches the critical value, f_c , where $f_c = cu_c$. As soon as this critical stage is reached and breakdown has started, the effective length embedded naturally decreases; the force required to extract the cord becomes less, and the region of breakdown travels back along the cord until separation is complete. Most conventional tensile testers will, therefore, record this maximum force as the pull-through force T_c , where $T_c = \pi r^2 F_c$.

Now F_c is obtained by putting the critical values in Equation (8), whence we obtain:

$$T_c = 2\pi r l f_c \frac{(\tanh nl)}{nl} \quad (9)$$

$$= \frac{k}{n} \tanh nl \quad (10)$$

where $k = 2\pi r f_c$.

This is the equation used in the main text, and the fit of experimental points to the hyperbolic tangent may be judged by referring to Figures 9 and 10.

PROBLEMS CONCERNED WITH THE PHYSICAL TESTING OF VULCANIZATES *

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INTRODUCTION

As early as the first session of the German Rubber Society in 1951 in Bad Neuenahr, it was urged that physical testing methods currently used in the rubber industry be reviewed critically and screened, and that guiding principles be formulated for future development. Thus Dr. Miedel, in a supplementary report, insisted that the uncertainty in abrasion tests should not merely be dealt with by means of a single example, but in a general and comprehensive manner, in order to gain a reliable judgment or to make possible useful conclusions for the rubber technologist, who is forced to make decisions regarding his compounding development on the basis of the results of the tests. In the Goslar meeting of the German Rubber Society in 1953, Dr. Kruse and E. A. Hampe posed the question of the value of dynamic testing methods, and the latter critic instigated a critical screening and systematization. Similar expressions of opinion can be found in the literature. It should be emphasized that, in the following considerations, we are dealing principally with the problem of the industrial rubber technologist, who has the task of examining and making reliable judgments on material which has been prescribed and is to be tested, with respect to its later application.

It must be pointed out that here testing problems are involved whose solution is a limited one or has a definite direction, but nevertheless one which is still by no means to be considered as solved. In a comprehensive presentation of the problems it is unavoidable that the considerations advanced are not new to every reader and they may have already been given thorough consideration.

THE FUNCTION OF TESTING

Every industrial test is concerned with production and the testing stems from the ultimate wish to improve the existing production.

Three different aspects of the role of physical and technological testing can be distinguished. The first and simplest task is that of the *control of materials*, or, more precisely, of *processing*. Here it can be a question, for example, of the control of raw materials or of control tests of mixtures of raw materials. The test results obtained in the use of a raw material or of a process must fall within definite limits. These are given by the variation of the test methods and the variation in the material. Without its being explicitly stated, it is of course basically assumed that any changes in the test material which will lower the quality of the resulting product will be caught by the test. By screening out material whose test results lie outside of the tolerance, a quality level is ensured

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by D. W. Kitchin from *Kautschuk und Gummi*, Vol. 8, No. 5, pages WT 117-124, May 1955; No. 6, pages WT 157-160, June 1955. This paper is based on a lecture given at the meeting of the German Rubber Society in München, October 21-23, 1954.

in the end product. It can be said that the test methods in general accomplish this task, provided the laws of statistics are sufficiently observed.

Also for judging a production process with a given compound, for example, a vulcanization process (determination of the optimum cure), available test methods are satisfactory for the most part. All the characteristics arrive at the values considered most favorable at more or less the same degree of vulcanization, although it is known that approximately the maximum values of tear resistance coincide with the maximum values of the tensile strength, but dynamically optimal properties later.

The testing of the unvulcanized mixtures with regard to their processability (for example, scorch, extrudability, tack) is not discussed in this paper, since we confine ourselves to the testing of vulcanizates.

In both the intended tests, compounds are compared that are identical or at least supposed to be identical, so that identical material structure is presupposed. By the test for the material control, the same structure of the vulcanizate is supposed to be reliably reproduced over and over again, since it is known from some experience or other that this structure will prove to give a satisfactory product even for meeting quite different requirements during later use. In the case of the determination of optimum vulcanization likewise, identical material structure is presupposed, and this is expected to be treated to best advantage by correct vulcanization. (By the correct vulcanization, the compound is made to manifest its best characteristics.)

The principal aim of the testing of vulcanizates is to determine which among a given number of different vulcanizates (different with respect to composition, vulcanization, or some other feature of processing) will turn out to be the most satisfactory for some particular later application. This is, therefore, *testing for compound development*. This is where the difficulties and problems begin. Whereas in the previously outlined acceptance tests the comparisons are made only on identical material with the same structure, in the testing for the development of improved compounds this is not the case. In this case it is necessary to evaluate materials of different compositions and consequently having different structures, with respect to the required future satisfactory performance.

No one presumably would be willing to predict from the duration of a life test in the laboratory a definite life in service. Nevertheless it is frequently the case that the results of the laboratory life test, together with the results of other test methods are utilized for the evaluation of the mixtures employed, and the compound with the longer life is considered to be more suitable. However, there is no certainty of the validity of this conclusion. There are various reasons for this. It is also seldom expected that the relative differences in the test results for different mixtures actually stand in the same relation as in the series in the later use. It is, however, often assumed that the order will at least agree in principle. Actually, however, there is no justification for any sharp separation between these two conclusions; both are equally certain or uncertain, as the example in Figure 1 shows.

Figure 1 shows the result of a destructive test of carbon black compounds in the St. Joe flexometer¹, where the life is a function of the magnitude of the alternating stress. The investigation shows the different behavior of two compounds with HAF carbon black compared with a compound with SAF carbon black and one with Corax L. The order of the compounds according to their life is dependent on the particular magnitude of the load at which the comparison is carried out. At large alternating stresses of 22 kg. and more, the compounds with furnace blacks can practically not be distinguished from each

other. At a load of 19 kg., the compound with SAF carbon black lasts twice as long as the compound with Vulkan-6, whereas the one with Philblack-O falls between them. At an alternating stress of 17 kg., the compound with Philblack-E is better by a multiple (theoretically infinite) than the compounds with HAF blacks. Here there is a reversal in the order of Philblack-O and Vulkan-6. Thus, according to the chosen load, different relative relationships and orders of quality are obtained. It is seen that between correct, correct "in principle", and incorrect ordering of these compounds, there is a fluid transition, so that no basic differentiation can be made in the certainty of the evaluation. The test conditions must, therefore, be so chosen that, from the test results, correct conclusions can be drawn with respect to the qualitative ranking of the compounds with respect to their satisfactory performance in service.

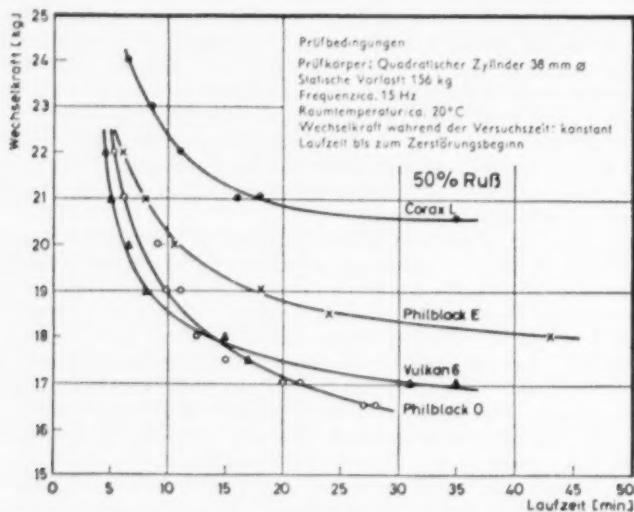


FIG. 1.—Dynamic destruction σ / (alternating stress). Rubber vulcanizates containing 50 per cent carbon black (on the rubber). Testing conditions:

Temperature: room at about 20°C.
 Test-specimen: square cylinder 38 mm. diam.
 Initial static load: 156 kg.
 Stress: alternating.
 Frequency: 15 cps.
 Duration: test carried to destruction.

The ordinate indicates the alternating stress in kg.; the abscissa the duration of the test in minutes.

STATEMENT OF THE PROBLEM

This paper investigates the problems of the physical testing of vulcanizates from the following points of view:

1. To what extent do test methods take into account the individual fundamental characteristics of the material, and to what extent combinations of different properties?
2. What relationships exist between the results of different test methods, and to what extent can these be explained by referring back to the same basic characteristics?

3. How can errors in test results be exactly described, and what is the reliability of such statements?

4. To what extent can conclusions drawn from the results of a test method be applied to the later application of the material?

CRITICAL STUDY OF TEST METHODS IN GENERAL USE

Alfrey² has represented the behavior of high polymers under dynamic loads (static load forms a limiting case of this, with very low frequency) in a comprehensive manner and described it in detail by means of models. Scheele³ has reviewed this work, with extensive commentary. In this paper it can be touched on only so far as this is necessary for a critical evaluation of the test methods.

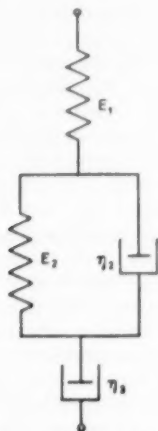


FIG. 2.—Model of the mechanical behavior of high polymers when deformed (according to Alfrey²).

A simple model for demonstrating the mechanical behavior of vulcanizates must be capable of showing elastic behavior, viscous flow, and damping. Figure 2 gives an example. It comprises a spring with modulus E_1 , connected to a damping member, represented by a Voigt model, with elasticity E_2 and dynamic viscosity η_2 , to which is attached dynamic viscosity η_1 for representing viscous flow. The deformation x produced by an external force S is calculated from the individual deformations of these parts, which are affected in a different manner by the duration t of the process, namely:

$$x = \frac{S}{E_1} + \frac{S}{E_2} (1 - e^{-t/\tau_2}) + \frac{1}{\eta_1} \cdot t$$

Here $\tau_2 = \eta_2/E_2$ signifies the relaxation time of the Voigt model. It goes without saying that, for a really accurate description of the behavior of vulcanizates, these individual elements in turn have to be still further resolved. As a first step it is to be assumed that E_1 is much greater than E_2 , and η_1 much greater than η_2 . The deformation with constant external force or the development or the decay of stresses will in each case depend on the ratio of the duration t of the test to the relaxation times of the material. In the case of very rapid and very slow processes, the behavior depends on the duration of the test.

With intermediate times, the separate mechanisms contribute in different ways to the total behavior. With constant deformation velocity, there results a stress S :

$$S = E \cdot x + \eta \cdot \frac{dx}{dt}$$

Of course these processes influence all subsequently applied test methods.

TENSILE STRENGTH

In the case of the tensile strength, therefore, the measured stress depends on the rate of elongation of the moving sample. At higher speeds higher stresses occur. Since the modulus E and the viscosity η change markedly with temperature, the test is also temperature dependent; in particular η decreases at higher temperature. It must be pointed out that in a tensile test, besides these influences, the tensile strength is only determined in part by the great number of the cohesive mechanisms, that is, by the average of the properties of the material, but principally by the structural "defects" in the broader sense. These do not come into play in the determination of the behavior of the material under slight loads. The distribution of the stresses in the material at the same external force depends on the form of the test sample, inasmuch as an ideal uniform stress distribution over the whole cross-section is never attained. Ring samples give lower tensile strength values than strip samples. Calculating the stress on the basis of the original cross-section is, to be sure, general practice in rubber testing, but it is evident that, in a material with greater elongation, there is a greater load per unit cross-section at the same absolute stress than at lower extension, so that, for an actual comparison of the tensile strengths, the tensile product should be employed⁴.

The forces which prevail at rupture are very large and depart markedly from those which occur in service, so in this test quite different cohesive mechanisms are involved. The same considerations apply to the stress values at high extensions.

HARDNESS OR SOFTNESS

The values measured as Shore hardness or DVM-softness characterize the resistance of the material to deformation of the surface. Depending on the duration of the indenting, the modulus of elasticity and the plasticity (dynamic viscosity) become involved. The frequency amounts to about 0.1 to 0.3 cycle per second. The reproducibility of the method has been greatly improved over earlier test methods by the standard DIN 53,505 of October 1951. In comparison with the United States standard⁵ there is a significant improvement in that the length of the needle which projects outside of the contacting surface is exactly defined. This is very important, and it has enabled us to obtain a significant improvement in standardizing the apparatus of our firm. Soden⁶ has pointed out that Shore hardness measurements are perhaps so popular because, as a consequence of their lack of sensitivity, there is little spread in the results.

RESILIENCE

Resilience is widely but quite improperly designated as elasticity. One should at least say resilient elasticity. It has already been defined by Memmler and Schob⁷ as the elastic efficiency of recovered work over applied work in percentage of the applied work. The impact process can be conceived as a half cycle, in which the vibration frequency amounts to about 50 to 100 cycles per

second⁴. The results are closely related to the modulus of elasticity and the dynamic viscosity of the material, as will be shown later on.

ABRASION

The abrasion methods described are combination tests which attempt to simulate the requirements of the intended service. It must be kept in mind that the test procedure according to DIN 53,516 lasts only 2.5 minutes and that over a distance of only 40 meters a readily measurable volume loss will occur. How great is the intensification of the destructive conditions and what guaranty is there that this intensification will be uniformly applied under all test conditions, so that there will still be a proper simulation of actual service? We shall not go into the manifold difficulties; in recent times they have been the subject of numerous investigations⁵. We have got the impression that it will not be possible to simulate the complex process of abrasion on the road in a single laboratory accelerated test, and by means of a single accelerated test to obtain the same order of quality among different compounds, as, for example, in a road test of tires. We have already discussed elsewhere how probably the only way to arrive at a useful evaluation is to combine the results of different appropriate tests of the individual decisive properties into a numerical measure, and yet test the characteristics one at a time.

TEAR RESISTANCE

It is difficult to find a satisfactory definition of this property in the literature. The German Standard DIN 53,507 defines tear resistance as the "resistance to further tearing of a notched rubber sample". The ASTM in its Standard D 624-48 does not explain tear resistance in any more detail. The British Standards 903 define the tear resistance as "the force which is necessary to produce further tearing in a cut in a rubber sample by traction on the rubber, where the force is principally normal to the plane of the cut". Busse⁶ explained tearing as "the formation of new surfaces under the action of a weak force, in which this is concentrated at the end of a sharp notch or cut in the sample". Apparently that property of the material is to be understood by which it can tolerate tensions which in a locally limited region considerably exceed the tensile strength determined for large cross-sections. A material which is designated as tear-resistant has the property either of dissipating local stress conditions by flow or by orientation in the region of great stress to form, before rupture, a structure of greater tensile strength than in the case of the ordinary rupture process.

The choice of the expression "structure strength" (Strukturfestigkeit) is not a fortunate one. Any material in the supermolecular range in which we are interested must have some definite order state or structure, and any type of destructive action involves an alteration of the structure apparently long before the onset of any change in the material. Even in breakdown tests (Zermuerungs-Pruefungen), this is not conceivable in any other way.

According to our experience it seems justified and meaningful to speak of a resistance to initial tearing and a resistance to further tearing and to develop suitable methods to distinguish between them. We have found that, when materials are rated in the order of excellence according to the results of a test of secondary tearing (previously damaged sample), they often come out the opposite way in tests of initial tearing (undamaged sample).

Ecker¹¹ has investigated the problem of what criteria can be utilized for

evaluating a tear resistance test. He found that, because of the high deformability of rubber, the applied force very soon is distributed over the whole cross-section of the rubber sample, so that the end result is that it is not the tear resistance that is tested, but the rupture strength. The true tear resistance is found when it is possible to exclude the elongation of the material. We have, independently, defined as coming closest to the purpose of the measurement that method which, calculating the measured absolute value on the original undamaged cross-section of the sample, differs most from the test for tensile strength. In so doing we have found, in agreement with Ecker, that this is best met by the ASTM Standard D 624-48 Form C (Figure 3). Moreover,

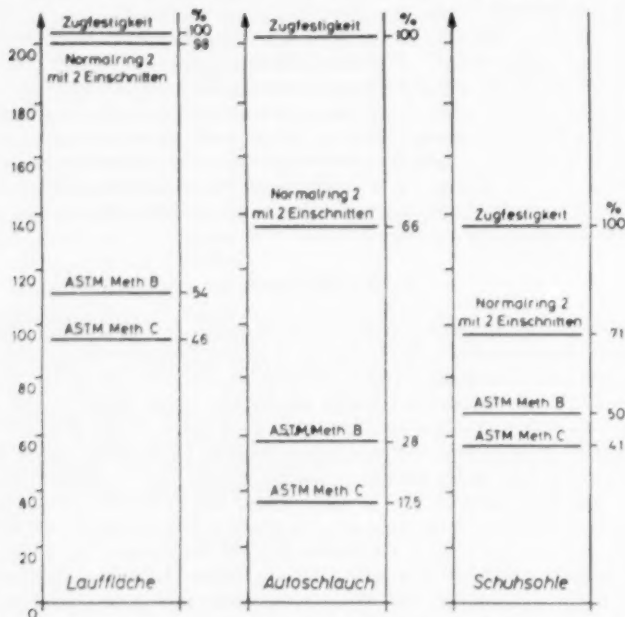


FIG. 3.—Deviation of the tear strength from the tensile strength for different test methods¹¹. The tensile strength is based on the cross-section of the unstressed test-specimen¹². The left-hand diagram is for a tire tread; the middle diagram is for an inner tube; the right-hand diagram is for a shoe sole. On all diagrams, *Zugfestigkeit* indicates tensile strength; *Normalring*, standard ring; *mit 2 Einschnitten*, with two incisions.

such a sample tears even at the slightest extension, as a result of the break which starts at the very least total stress, so that accordingly the criterion of Ecker for a correct tear test is fulfilled.

It is easy to see that the tear resistance, described as the ability to withstand high local stresses, is extremely dependent on the sample shape, since this determines the stress distribution, as Angioletti and other authors have demonstrated¹³. Graves postulated as the most correct test for tear resistance that method in which the greatest stress concentration is reached¹³, which can be demonstrated by photoelastic methods.

The ability to withstand stresses or to dissipate them depends on the modulus of elasticity and the dynamic viscosity of the material. These properties depend on the velocity and on the temperature, so that the tear resistance values are strongly influenced by the test conditions.

DYNAMIC TEST METHODS

It has been recognized that the above mentioned test methods are not sufficient to simulate the behavior of vulcanizates for the especially complex requirements in tires, spring elements, and similar applications. In "static tests", it generally is a question of a single process, with a gradual increase to a high degree of tension. In dynamic test methods, small and rapid alternating forces act on the vulcanizate. These latter methods are frequently also better than the static ones for bringing out smaller differences in the compounds.

Basic for the dynamic test methods are the ideas concerning the physical characteristics of the vulcanizates and the concepts which have been developed for these. Dillon and Gehman¹⁴ have made a systematic survey of all test methods which have been employed for the measurement of dynamic properties. The methods depend on free or forced oscillations, and in the latter case also a distinction is made between resonance methods and measurement outside of the resonance region.

The test methods which use free oscillations are based on the measurement of the decay of oscillation processes. Thus, for example, a torsion pendulum is given an initial displacement, and the successive amplitudes of swings are measured. It is not easy to carry out an exact measurement of the magnitude. The method has other fundamental defects. The decay of the amplitude of oscillation has an effect on the dynamic viscosity which is being measured, since this magnitude depends on the amplitude of oscillation. The free oscillations have the natural frequency of the system. In general, the natural frequency of different samples is not the same, since it depends on the dynamic modulus of elasticity, so that the dynamic viscosity cannot be measured at the same frequencies. Yet the values depend on the frequency.

The methods which use forced oscillations employ a vibrating system which consists of a mass, a spring constant, and a damping element, and the two latter magnitudes should as far as possible come from the rubber sample itself. The system is excited by an external sinusoidal alternating force, produced either electrically or mechanically, into a state of resonance oscillations. By varying the mass, various frequencies can be traversed, so that the values to be measured for different samples can be obtained by interpolation for the same frequency. However, a wide frequency variation is not possible. The methods of forced vibrations outside of resonance either record the force-path diagrams automatically or they operate by detuning of vibrating systems by simultaneous vibrations of the rubber samples. The last named methods can run through a very wide frequency range.

Attempts to standardize the different methods are at present under way in the United States. This is difficult, since it is first necessary to clarify the concepts on which the methods are based. Marvin¹⁵ has incidentally proposed nineteen different methods for a comparative test.

It has already been stated that the dynamic numerical values characterize the material only for the test conditions under which they are obtained. Hence one finds dependence on frequencies, temperature, previous stresses, and the magnitude of the alternating load, as has been frequently demonstrated¹⁶. Testing over different temperature ranges is current practice in Germany, and it should be pointed out that in general the dynamic viscosity in the range from about -30°C to 100°C decreases with increasing temperature, so that fortunately the material, which tends to heat up due to energy absorption, does so less and less. Probably less well known is the dependence on the frequency and the magnitude of the load. These too have in recent times been investi-

gated over very wide ranges for the most diverse elastomers¹⁷. Our own studies have shown the same (Figure 4).

From the dynamic viscosity and the dynamic modulus of elasticity one can calculate the hysteresis and the energy absorption per complete cycle in the precise sense, and from that then the amount of heat developed. By taking into consideration the heat loss by conduction, one can calculate exactly the relationship between the temperature evolutions to be expected and the proper ordering of the compounds, as Oberto and Palandri¹⁸ and the present author and Haendler¹⁹ have shown. We have pointed out in detail¹⁶ that it is essential to ascertain, at least qualitatively, the nature of the demands of service and to choose the test conditions accordingly. The further improvement of the dynamic test methods and their evaluation presupposes, therefore, that the

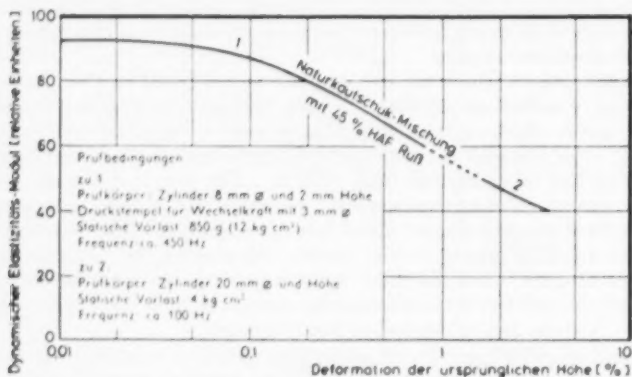


Fig. 4.—Change of dynamic modulus of elasticity with the amplitude of the vibration (compression). Testing conditions for (1):

Test-specimen: cylinder 8 mm. diam., 2 mm. high.
Piston for alternating stress: 3 mm. diam.
Initial static load: 850 g. (12 kg./cm.²).
Frequency: 450 cps.

Testing conditions for (2):

Test-specimen: cylinder 20 mm. diam., 20 mm. high.
Initial static load: 4 kg./cm.².
Frequency: about 100 cps.

The ordinate indicates the dynamic modulus of elasticity (relative units); the abscissa the percentage deformation from the original height.

magnitudes occurring in the service demands become known or that more exact ideas be gained concerning them than is at present the case. This is especially true for tires, and every effort should be made to find out definitely how great are the deformations and the forces in the individual parts of the tire cross-section. It must be theoretically possible, with sufficient knowledge of these quantities, to set up an energy balance for a given tire and to calculate the relative contributions of the tread, carcass, (rubber and cord) etc., to the heating of the whole tire.

The electrical test methods which have been described in many different places, and which have been reported by Krug²⁰ and Kickstein²¹, show in their definitions analogies with the mechanical magnitudes, a fact to which attention has been called by Wolf²², for example. The merit of the measurement of electrical properties consists in the better insight they give into the structure of

the material, particularly in the case of semiconducting carbon-black compounds, which are used currently in ever greater amount, as well perhaps as the help they afford in studies of dispersion of fillers. However, to date it has not been possible to draw any useful conclusions about the decisive mechanical properties from the electrical properties.

REPRODUCIBILITY AND SPREAD OF THE MEASUREMENTS

The necessity of overcoming wide variations has arisen because of the progress in industrial research. It is not sufficient in the rubber industry to seek the causes of errors chiefly in errors in the methods of measurement. Between the idea of the compounder and the results furnished by the tester there is a succession of processes which introduce marked variations, and thus all contribute to the presence of errors in the end result.

For the description of these variations, statistics has been fundamentally expanded and developed, chiefly by English investigators, to meet the needs of natural scientists and engineers. These statistical methods frequently make it possible to answer questions which previously could not be answered²³. Within the limits of these discussions, we can only give a few examples of the variance of test results. To avoid misunderstandings, it must be emphasized here that mathematical statistics cannot remove the variances but merely describe them exactly and guard against false conclusions in the evaluation of the test results. It is self evident that, as much as before, it is still one of the duties of the tester to be concerned with the most closely controlled mixing, exact vulcanization, and exactly prepared test samples, and to be scrupulous about the accuracy and the sensitiveness of the test apparatus.

The value of statistical methods can be demonstrated by an investigation of the influence of atmospheric conditions on the results of the De Mattia test with perforated test samples (crack growth). The previously aged samples (tire tread) were first punctured, then stretched in the machine, and the time measured that was required to form a split of 1/2 inch. The testing was carried out both on the roof of the laboratory building (where the samples were sheltered from rain and direct sunlight) and indoors. The results were as follows:

Sample no.	Sample life in minutes	
	Series I Indoors	Series II Outdoors
1	520	480
2	525	490
3	530	510
4	540	500
5	515	470
6	550	495
7	520	520
8	530	485
9	540	505
Average	$\bar{x}_1 = 530 \text{ min.}$	$\bar{x}_2 = 495 \text{ min.}$
Mean square deviation	$s_1 = \pm 11.4 \text{ min.}$	$s_2 = \pm 15.6 \text{ min.}$

The question now arises, whether this difference between the two series can actually be attributed to various atmospheric influences or can be explained by errors in test methods and variations in the material.

It should be noted that the answer to the question of the magnitude of the variance of the series of measurements depends on the number of test samples (a large number of samples gives a better indication of the variance) and also finally on the degree of certainty with which one wishes to make an assertion. The choice of this certainty is of course arbitrary, yet in practice it has proved to be the case that, in general, a statistical certainty of $S = 95$ per cent is satisfactory. This means that with very many repetitions of the series of measurements one can expect in 95 per cent of all repetitions that the same outcome will be obtained. It is an advance in mathematical statistics that it is no longer necessary to carry out series of measurements with, say, one hundred individual tests in order to obtain a reliable result. The possibility of a non-Gaussian distribution for a small number of samples has been studied and tables of functions have been worked out for such a case. This t function depends, not only on the number of tests performed, but also on the statistical certainty demanded. Although the derivation cannot be given here, the two mean values are to be evaluated according to the following formulas:

$$s_d^2 = \frac{s_1^2(N_1 - 1) + s_2^2(N_2 - 1)}{N_1 + N_2 - 2}$$

$$t = \frac{\bar{x}_1 - \bar{x}_2}{s_d} \cdot \sqrt{\frac{N_1 \cdot N_2}{N_1 + N_2}}$$

where \bar{x}_1, \bar{x}_2 are the mean values of the individual test series,

s_1, s_2 are the mean square deviations,

N_1, N_2 are the number of samples.

The calculation in our case gives a value of $t = 5.40$, which according to the t function corresponds to a certainty of more than 99.9 per cent. This states that the difference between the two mean values is so certain that, with 1000 repetitions with 9 samples each, it would be found again in more than 999 cases, or, from a practical point of view, the difference is to be attributed with certainty to various atmospheric influences and cannot be explained by errors in the test results.

A further example will serve to show what this method accomplishes. In another case the vulcanized unaged De Mattia test strips likewise from a tire tread compound were perforated, and the subsequent tear measurements made outdoors and indoors. We obtained the following results.

Sample no.	Sample life in minutes to 1/2-inch splitting	
	Series III Indoors	Series IV Outdoors
1	390	480
2	500	445
3	480	495
4	455	360
5	500	420
6	460	360
7	460	430
8	495	390
9	470	490
Average	$\bar{x}_1 = 468$ min.	$\bar{x}_2 = 430$ min.
Mean square deviation	$s_1 = \pm 34$ min.	$s_2 = \pm 51.6$ min.

To evaluate the certainty of the difference, the variance of the difference $s_d = 43.7$ was computed and, from this, $t = 1.84$ calculated. The tables for t show that the certainty of the difference between the two mean values is less than 95 per cent, that is, that the difference may possibly be attributed to the spread of the test results. Since the function depends on the number of samples, as well as on the certainty required, it may be asked how many samples must be chosen when a test is repeated in order to settle the problem. If, in this connection, it is first assumed that the range of variation just found will not change when the test is repeated, then from the formula for t , a value for $N_1 = N_2$ can be calculated. In our example, it would be necessary to repeat the experiment with 12 samples. It would be preferable to choose more samples, say 15, in order to take into account a change in the variance.

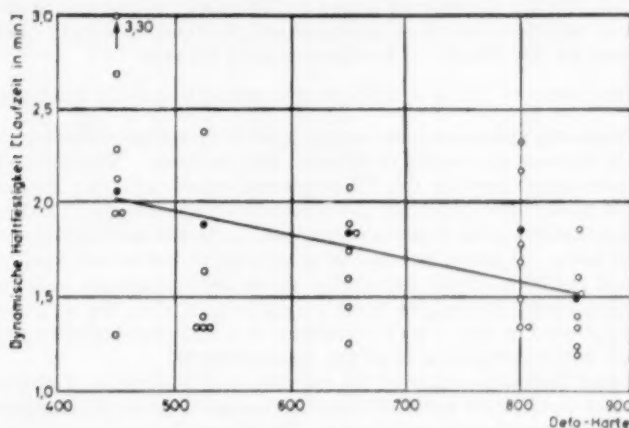


Fig. 5.—Dependence of the dynamic adhesion on the Defo hardness of a natural-rubber carcass compound containing SRF black.

Adhesion = $2.62 - 0.001 \quad 254$ Defo hardness.
Cord 1650/2 stretched.
Correlation coefficient $r = -0.39$.

The ordinate indicates the dynamic adhesion (time in minutes); the abscissa the Defo hardness.

The important point is that, with the help of these methods, a better planning and evaluation of experiments is possible than was previously the case²³. Buist has shown this in connection with the design and performance of the comparative testing of the International Standards Organization for the abrasion tests with the du Pont machine²⁴. Mandel and coworkers have given a similar demonstration in the planning of the road tests of tires carried out by the Bureau of Standards²⁵.

RELATIONS BETWEEN THE RESULTS OF DIFFERENT TEST METHODS

Statistical methods are also useful for bringing out the relationships between various properties. These functions are, to be sure, formulated, not according to their physical content, but according to the laws of probability. Buist and Davies²⁶ has given a number of examples of the application of these methods. We have investigated, for example, the dependence of the adhesive properties of cord-to-rubber on the degree of mastication of the uncured compound applied

under pressure (see Figure 5). The marked scattering of the values of the adhesion would presumably not allow any evaluation of the results.

If one first assumes a linear relationship then the straight line through the field of points must take into account the scattering of the values. The statistical method gives the simple linear regression equation:

$$\text{Adhesiveness} = 2.62 - 0.00125 \text{ Defo hardness}$$

In each case it must be ascertained whether such an equation applies. The regression coefficient indicates what average change is to be expected in the adhesiveness when the Defo hardness of the pressed on compound changes by 1 unit.

The regression equations can also be extended to a number of properties; for example, like the dependence shown by Thornley²⁷ of the road wear of tires (in order of merit) on the Shore hardness and the tensile strength of the compounds used for tire treads. The equation is as follows:

$$\text{Road wear} = -36.4 + 0.912 \text{ tensile strength} + 0.431 \text{ hardness}$$

The linear regression can also be employed to investigate whether there is a correlation between the results of different test methods. The study of such a possible correlation between the different test methods affords a deeper understanding of the test process and of the demand on the material. The knowledge of the relationship makes possible a judgment as to the informativeness of the individual tests. It provides a means of arriving at better and more precisely defined test methods. Such knowledge about the information value of a test method is necessary for judging what weight to give when the results of a test are to be included in the overall evaluation of a compound quality within the framework of the indications of all the measurements.

Buist and Davies investigated the correlation of the results of physical tests on tire-tread compounds with different blacks and different filler contents and calculated²⁸ the correlation coefficient r . By this coefficient is meant a measure of the accuracy of the correlation between two or more quantities, which can be measured in any case only with more or less scattering and between which, as a first approximation, there is a linear relation of the nature of:

$$y = a + bx$$

The value of this coefficient lies between -1 and $+1$. For $r = +1$, the linear relation is exact in the above form and y increases with x . For $r = -1$ y decreases with increasing x . For $r = 0$ there is, in general, no correlation between the two series of measurements. The correlations found by Buist are given by Table 1.

Budd and Larrik²⁹ studied the results of various life tests on cord and calculated the correlation coefficients for them in a similar manner.

When two test methods have a high correlation coefficient, this indicates that they are measurements of closely related properties of the material. Those methods which show no relationship are testing different properties of the material. The qualifying statement must be made, however, that this is strictly the case only provided that, in both cases, the magnitudes of the severity of the treatments are the same, or at least similar.

The correlation coefficient r is related to the regression coefficient, but this will not be further pursued here, since the theory shows r^2 is a measure of the relationship between the variance of the two or even more investigated values.

TABLE 1
CORRELATION BETWEEN DIFFERENT TEST METHODS ON NATURAL RUBBER MIXES
WITH DIFFERENT BLACKS AT VARIOUS LOADINGS

	Abrasion ¹	Tensile	Elongation	Shore hardness	Resilience at 50° C	Modulus at 300%	Detrition temperature ²	Dynamic resilience ³	Dynamic modulus	High freq. modulus	Plasticity ⁴	Torsional resilience ⁴
Abrasion ¹	1. —	-.291	+.498	-.729	+.417	-.625	-.061	+.462	-.584	-.576	-.453	+.491
Tensile	-.291	1. —	+.316	-.258	+.462	-.114	-.390	+.399	-.424	-.361	-.290	+.534
Elongation	+.498	+.316	1. —	-.847	+.355	-.965	+.125	+.351	-.631	-.501	-.309	+.538
Shore	-.729	-.258	-.847	1. —	-.716	+.860	+.255	-.720	+.877	+.835	+.673	-.817
Hardness												
Resilience at 50° C	+.417	+.462	+.355	-.716	1. —	-.330	-.832	+.963	-.848	-.942	-.922	+.948
Modulus at 300%	-.625	-.144	-.965	+.860	-.330	1. —	-.167	-.333	+.612	+.503	+.323	-.499
Detrition temperature ²	-.061	-.390	+.125	+.255	-.832	-.167	1. —	-.821	+.543	+.647	+.720	-.690
Dynamic resilience ³	+.462	+.399	+.351	-.720	+.963	-.333	-.821	1. —	-.908	-.922	-.818	+.936
Dynamic modulus	-.584	-.424	-.631	+.877	-.848	+.612	+.543	-.908	1. —	+.905	+.689	-.936
High freq. modulus	-.576	-.361	-.501	+.835	-.942	+.503	+.647	-.922	+.905	1. —	+.901	-.954
Plasticity ⁴	-.453	-.290	-.309	+.673	-.922	+.323	+.720	-.818	+.689	+.901	1. —	-.834
Torsional resilience ⁴	+.491	+.534	+.538	-.817	+.948	-.499	-.690	+.936	-.936	-.954	-.834	1. —

¹ Du Pont abrader. The German test refers to this as the Dunlop abrasion machine.

² Ball test, 25 kg. Temperature after 1000 revolutions.

³ Falling weight, 1000 g. Temperature after 1000 revolutions.

⁴ Williams' torsion pendulum. Resilience R (%) = 100 - damping, determined as the leveling off of free oscillation.

⁵ Same as note 3 but for the torsion pendulum.

In the example of the dependence of the adhesion cord-rubber on the degree of mastication of the carcass compound, the correlation coefficient $r = -0.39$. This means that only 15 per cent of the deviations of the adhesion can be attributed to deviations of the Defo hardness of the compounds employed; the far greater remainder is to be sought in other causes. In the case of the multiple regression calculated by Thornley between road wear on the one hand and tensile and hardness of the tread compound on the other, the correlation coefficient amounted to $r = 0.913$. This indicates that about 80 per cent of the total deviations in the ordering according to quality of the tire compounds with respect to their road wear are to be attributed to the mutual influence of hardness and tensile strength, or to some property underlying both of these. The residual deviation is due to the variance of the test method of road wear or to other influences which are not contemplated in the test.

The researches on the formation of multiple regression equations or multiple correlation coefficients indicate the possibility of replacing the unsatisfactory complex test methods, such as the abrasion test, by an exact combination of the results of the measurement of individual properties, and thus of making progress in this field.

The methods of mathematical statistics describe the relationships between different properties only on the basis of the test results obtained and their variance. They are valid, therefore, only in the range studied and only with a certain reliability. They look at the correlation from the outside, so to speak, instead of from the point of view of physical content. It is conceivable that, even with very high correlation, there is no immediate connection between two properties. These might rather, for example, be related to each other indirectly through a third property which underlies the two measured quantities. For this reason statistical relationships are valuable as an indication of actual interrelations of a physical nature. The search for direct physical relationships and laws is thus by no means rendered superfluous by the statistical methods.

We include two more examples of investigations of this sort, to which we have already referred previously¹⁶. They deal with the relation of the dynamic properties of vulcanizates to several test methods in current use in Germany. The indicated relationships have been studied by us with additional compounds, for which we here give the results.

REBOUND RESILIENCE

The relationship has already been derived¹⁶. The process of deformation in the rubber sample is pictured as a semivibration or half cycle. For the resilience R the following gives the value:

$$R_I = e^{-\pi\eta\omega/E}$$

or as a series approximation:

$$R_I = \left(1 - \frac{\pi \cdot \eta \cdot \omega}{E}\right) \cdot 100\%$$

In this expression E is the dynamic compression modulus, η the dynamic viscosity, and ω the angular frequency, which in this case is calculated from the duration of the impression.

As the formula shows, the resilience increases with increasing modulus of elasticity and decreases with increasing dynamic viscosity. It is also known that the resilience can be used as a measure of the hysteresis of compounds

when the samples are of equal hardness. The pronounced dependence of the dynamic viscosity on the temperature also explains the temperature dependence of resilience. Figure 6 shows the relationship between the values calculated from the dynamic properties by the above approximation formula. In order to deal with a sufficiently large range, it was necessary to employ compounds of widely different character. The agreement can be considered good, although the calculation with the above mentioned assumptions gives values that are somewhat high. This is perhaps to be attributed to the fact that the deformation of the sample goes past the equilibrium position after the pendulum

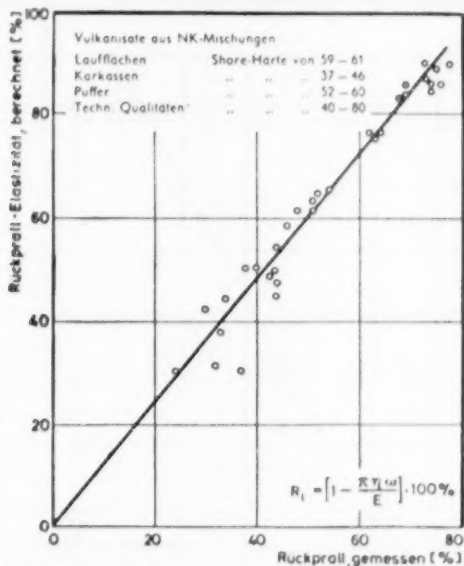


FIG. 6.—Relation between the dynamic properties and the rebound resilience. Measurements at room temperature by a Schob pendulum resiliometer. The results are calculated from the dynamic properties as a half cycle. The ordinate indicates the rebound resilience in percentage; the abscissa the percentage rebound. The legend on the diagram is as follows:

Natural-rubber vulcanizates.
 Laufflächen = tire tread.
 Puffer = cushion.
 Techn. Qualitäten = Technical compounds.
 Shore Härte = Shore hardness.

has rebounded, so that the whole process lasts longer than a half cycle. In this case the calculation would give smaller values and the agreement would be better.

DAMPING ACCORDING TO ROELIG

The percentage damping introduced into rubber testing by Roelig is not a simple fundamental property. The relationship to the dynamic properties according to our definitions has been derived in the foregoing¹⁶. One obtains for the relative damping in percentage the expression:

$$D = \frac{200}{1 + (2E/\pi^2 \cdot f \cdot \eta)} \%$$

where E is the dynamic compression modulus, η the dynamic viscosity, and f the frequency. By more recent calculation of the example given earlier, the relationship in the region of intermediate damping has been somewhat improved (see Figure 7), yet there remains a considerable discrepancy at the higher damping values. This is presumably to be ascribed to the dependence of the modulus of elasticity on the magnitude of the load as well as on the different sample shapes in the two test procedures. The form factor has an especially great influence on the compression modulus and the smaller sample shape in Roelig's study (slabs 4 mm. thick and 40 mm. width) gives a higher modulus than our test samples (square cylinder of 20 mm. height and diameter).

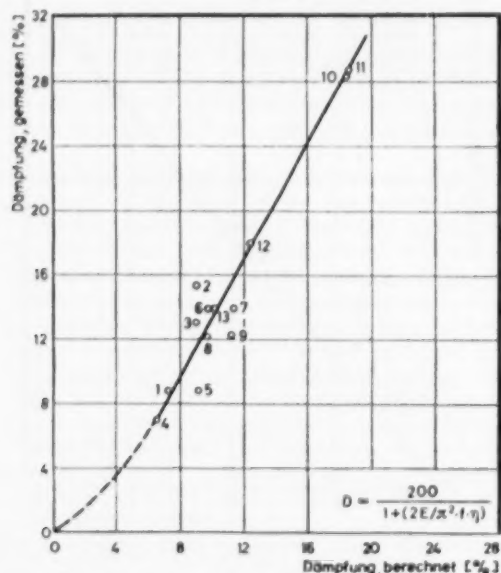


FIG. 7.—Percentage damping by the method of Roelig, measured and calculated from the dynamic properties. The compounds are those of Kainradl and Haendler¹⁴. The ordinate indicates the measured damping; the abscissa the calculated damping.

PREDICTIONS ABOUT SERVICE QUALITY FROM THE RESULTS OF LABORATORY TESTS

It is evident that, in any development of test apparatus, the intention is to make it possible to draw conclusions as to the suitability of the tested material for a specific application. It is well known in the case of many test methods that this goal is not attained. The tests are performed and then the comment is made that conclusions regarding the satisfactory service use are not possible. Thus, the International Standards Section in its recommendation for the abrasion testing with the du Pont-Grasselli machine determined²⁸ that the correlation with the road test results is to be sure faulty, nevertheless because of commercial reasons a standardization of the method should be carried out. Such a state of affairs can only be regarded as unsatisfactory. In particular,

the life tests should make possible estimates of the applicability of different compounds for a specific application.

LIFE TESTS

Thus the purpose of the Martens test apparatus for breakdown tests on cylindrical samples was to simulate the destruction of the material in massive (truck) tires. In spite of the identical load used in a comparison of different compounds, the test is by no means comparable with a definite service condition

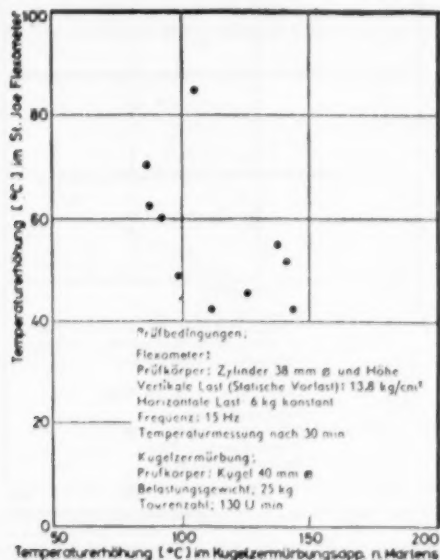


FIG. 8.—Temperature rise in the St. Joe flexometer, with constant alternating stress, and in the Martens breakdown tester. Tread compounds of natural rubber and "cold rubber" containing SAF and HAF blacks and different plasticizers. Shore hardness 47–66°. The legend on the diagram shows the test conditions:

Test-specimen: cylindrical 38 mm. diam. and height.
 Vertical load (static initial load): 13.8 kg. per sq. cm.
 Horizontal load: 6 kg. constant.
 Frequency: 15 cps.
 Temperature measurement: after 30 min.
 Ball breakdown:
 Test-specimen: ball 40 mm. diam.
 Load: 25 kg.
 Revolutions: 130 r.p.m.

The ordinate indicates the temperature rise in degrees Centigrade for the St. Joe flexometer; the abscissa temperature rise in the Martens ball breakdown apparatus.

under constant force, as we have already shown and propose to show again here on the basis of additional comparison material. Figures 8 and 9 give the results of comparative tests in the cylinder breakdown tester (Kugelzermübbungs-Pruefer) and in the St. Joe flexometer, with constant load and constant deformation. The relationship in the two cases is very poor, an indication of the undefined relationships in the cylinder breakdown test apparatus.

Depending on the magnitude of the deformation, the acting force, and the dynamic viscosity of the material, part of the applied mechanical work in breakdown tests of the above type, is converted into heat, and

this gradually leads to destruction of the material. In the comparison of different compounds with the same modulus of elasticity, it can, however, happen that some materials, in spite of greater heat development, last longer, so that, besides degradation by heat, a direct mechanical attack must be assumed¹⁹. The question arises as to which properties are decisive for this longer duration. Since rapidly alternating stresses (varying both in direction and magnitude) the decision must be made possible by a dynamic test of the tear resistance.

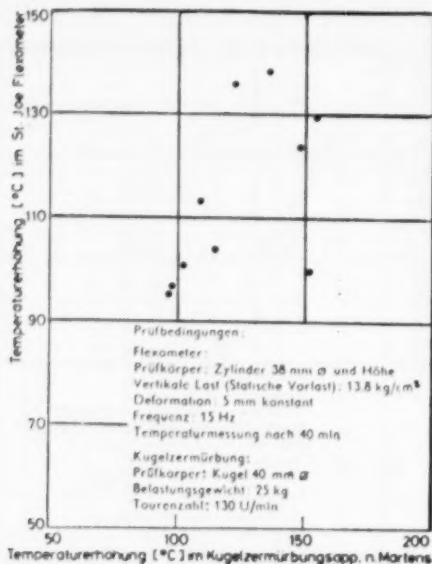


FIG. 9.—Temperature rise in the St. Joe flexometer, with constant deformation, and in the Martens breakdown tester. Tread compounds of natural rubber and "cold rubber" containing SAF and HAF blacks and different plasticizers. Shore hardness 47–66°. Test conditions:

Test-specimen: cylinder 38 mm. diam. and height.
 Vertical load (static initial load): 13.8 kg. per sq. cm.
 Deformation: 5 mm. constant.
 Frequency: 15 cps.
 Temperature measurement: after 40 min.
 Ball breakdown:
 Test specimen: ball 40 mm. diam.
 Load: 25 kg.
 Revolutions: 130 r.p.m.

The ordinate indicates the temperature rise in degrees Centigrade for the St. Joe flexometer; the abscissa the temperature rise for the Martens ball breakdown apparatus.

In this test the development of heat must be prevented as far as possible in order to measure the effect of a direct mechanical attack. Figure 10 shows the influence of the sample height on the temperature of destruction of vulcanizates under different test conditions. The lower test samples reach the same life periods at lower temperatures, in spite of the fact that they are exposed to greater alternating forces. By decreasing the height of the test-pieces, an appreciable shifting from thermal to mechanical causes was attained.

The determination of the end of the test must be carefully studied and defined. A careful observation shows that the material undergoes continuous change during the exposure. The flow (progressive deformation at constant

force) indicates a continuous alteration of the structure. This continuous change of properties could already be interpreted as incipient destruction. Since it can be borne for different lengths of time by different materials, it is seldom decisive for service life as long as it remains within certain limits. In deciding when the end of a life test should be considered to have been reached, one should regard even the slightest mechanical degradation (depolymerization by intense local heating, tearing, or wear) as an indication of this. In the case of a tire in particular, the occurrence of such local damage leads rapidly to complete destruction of the whole tire. On the other hand, in many fatigue tests with constant deformation, it turns out that by the early appearance of such a small damage the mechanical stresses at this place are markedly reduced.

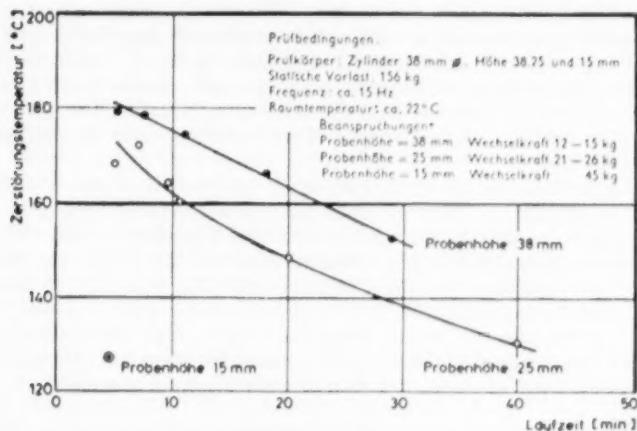


FIG. 10.—Effect of height of sample on the temperature of breakdown for the St. Joe flexometer. Natural-rubber tire tread containing 50 per cent by weight of HAF black. Test conditions:

Test-specimen: cylinder 38 mm. diam.; heights 38, 25 and 15 mm.
 Static initial load: 156 kg.
 Frequency: about 15 cps.
 Temperature: room at about 22° C.
 Applied alternating load:
 Height of specimen: 38 mm., 12–15 kg.
 Height of specimen: 25 mm., 21–26 kg.
 Height of specimen: 15 mm., 45 kg.

The ordinate indicates the temperature of breakdown; the abscissa the duration of the test in minutes. The legends on the curve indicate the heights of the test-specimens in mm.

The test-piece made of this compound is less severely exposed in the subsequent course of the test and, under certain conditions, can last longer than compounds which show later incipient destruction. In testing, therefore, precautions must be taken which will make the beginning of destruction clearly recognizable, and enable one to observe the change of the modulus of elasticity of the material during the whole test.

AGING TESTS

The methods for the artificial aging of vulcanizates often give different orders of quality in the compounds tested, and they often show deviations from natural aging. The procedures which have been proposed for artificial ozonization show little agreement in the results with natural aging as Schneider³⁰ has

shown. The apparatus employed to determine the bend-cracking resistance (Biegeriswiderstand) furnish for the most part results that are hard to reproduce and which compare poorly with each other.

Aging tests carried out in cabinets differ from later conditions in service principally in the absence of light and motion of the test-piece. It should at least be made certain to that the total volume of all the samples does not exceed a certain ratio to the volume of the cabinet. The International Standards Organization proposed a ratio of 1:10 as the upper limit. In ordinary aging of samples, it is possible that antiaging materials diffusing out of protected compounds may also tend to protect compounds which contain little or no antioxidant²¹. Furthermore, volatile oxidation products can be evolved from more rapidly aging compounds, so that, in the protected compounds, too a more rapid aging can occur. We have aged a natural rubber tire-tread compound with phenyl-2-naphthylamine, aldol resin, aldol powder, Nonox HFN, and 4010, alone and together with unprotected compounds, in the Bierer-Davis oxygen bomb. The free space in our experiments with a fully loaded bomb amounted to 30 times the sample volume, kept the same in each case. Nevertheless, we found several cases of a mutual effect. These results need to be confirmed by additional studies.

An essential defect in the static tests is the fact that they offer a stationary surface to ozone attack. The incorporated light-protection agents, in case a wax is involved, migrate to the surface and form a protective film. The test result becomes quite different if moving surfaces are exposed to the attack of atmospheric conditions, where any protective wax film that may be present is ruptured. For tests of this sort, three methods are known in practice: the du Pont chain test²², the De Mattia bend-crack test²³, and the outdoor flexing machine of Vanderbilt²⁴. In the two first cases, the dynamic loading is great and even in enclosed spaces destruction of the test-pieces takes place by crack formation.

A problem common to all aging test methods is the comparative evaluation of aged test-pieces which have undergone different forms of attack. The frequently proposed preparation of thin sections with accompanying integration of the remaining cross-section surfaces is probably out of the question, so that there remains no other recourse than visual inspection. We had good success with photographs of characteristic stages of deterioration. This method is standardized for the De Mattia test without perforation according to the British Standards 903²⁵. The method of evaluation of the BS 903 is noteworthy, and it has been employed by us with good success. The conditions of deterioration observed during the whole course of the test period are classified with the aid of these photographs and are all calculated back to an intermediate state by a method developed by Newton²⁶ on the basis of statistical investigations. The large spread in the test results are more easily overcome by this means.

In the bend-tear test, a distinction should be made between initial tearing and subsequent tearing. The statement made earlier holds, that within a series of compounds (tread compounds), compounds which tend to show initial tear often show greater resistance to subsequent tearing. For the test of the secondary tearing (De Mattia) the test-piece is perforated, for which purpose a small device was recommended by the International Standards Organization. We have made a thorough study of this test. The results show considerable dispersion if one uses the method of stressing at present prescribed in the United States²⁷ or in the British Standards²⁸, in which the stretched length of the

samples is greater than the elevation. The test strips thus remain in a bent state, and there is no change of direction of the stress. The test time is decreased by a power of ten and the relative scattering (*Variationskoeffizient*) reduced considerably if the stretched length is so chosen that it is equal to the greatest separation of the jaws.

A defect of the weathering tests is that the weather conditions which prevail during the test are always a matter of chance and at best can be only observed, not created. It would be necessary to investigate the climatic and meteorological relationships intensively over long periods and taking into account the necessary viewpoints with respect to rubber testing, in order to create the statistical bases for the definition of a "normal climate". We have determined the ozone content of the free atmosphere in Traiskirchen twice a day for a year, and found a monthly average of 1.65 to 3.36×10^{-8} parts by volume of ozone per unit volume of air. Individual peak values ranged from 5×10^{-8} to 8×10^{-8} , but the latter value was found only three times during the year of observation. The high ozone concentrations occurred frequently during a strong south wind (Foehn) or before thunderstorms, yet they were also found just as often without our observing any peculiarities in the weather. A standard climate defined on the basis of such observations would have to form the basis for the tests in a weathering cabinet similar to the ones that are used in the United States. Ford and Cooper²⁷ have given a detailed description of such a cabinet, which they constructed for investigations of aging, and employed with simultaneous dynamic working of the test samples. Hitherto the attempt to separate the mechanical deterioration from the attack by atmospheric agents has seldom been made. The influence of the atmosphere is very great as Kuzminski²⁸ has demonstrated.

A distinction has often been made between protection vs. aging and protection vs. fatigue. It has seldom been defined what is to be understood by this. If one expects to achieve a better capability of resisting deterioration caused by purely dynamic punishment and the accompanying heat development by the addition of an antiaging protective agent, then it must be exactly stated on the basis of what dynamic test this assertion is made. By the addition of a protective agent to the compound, a softening may be produced in the vulcanizate, so that this "protected" compound looks better in a test with constant deformation than a compound with higher modulus of elasticity. With a given strain, the softer compound will be under less mechanical stress. The De Mattia test, the du Pont chain bending test, the outdoor flexing test, and perhaps even the ball breakdown test are to be considered treatments at constant deformation. We have so far not been able to find that a compound protected vs. aging has actually attained a longer life in the flexometer.

THE CHOICE OF TEST METHODS

It would theoretically be desirable that the various conditions to which the completed article is to be subjected, and consequently the compound to be tested should be clarified qualitatively and quantitatively. It is self-evident that it must be distinguished whether the deformation or the alternating load is what is prescribed. Especially for tire compounds, it must be known how great are the shearing, the compression, and the tension forces, and how great the constant and the alternating load, and how high the frequency. In spite of the difficulties, every effort should be made to gain a better picture than we have of the demands on the material in tires. Angioletti²⁹ has shown how

photoelastic techniques can be applied to the investigation of the stress conditions in the field of rubber technology. Oppel³⁹ has also described the procedure for investigating stresses in tire cross-sections. Kern⁴⁰ has described the methods available for the study of the strain paths of the profile blocks of tire treads, and how the stress relationships can be ascertained in raised ellipses (Aufstandsellipses) of the tire. Further Loughborough and coworkers⁴¹ have concerned themselves with the stress relations of the cord in the tire. They attached wire loops next to individual cord strands at definite distances apart and determined these distances with x-rays after the tire was pressed off. We have used strain gauges to measure the stresses of the innermost layers of cord in the slowly rolling tire. It must be attempted to apply the measurements to tires running at high speed. During the war, Brunner⁴² measured the temperature continuously in a tire on a moving automobile.

In practice, of course, the testing of compound development cannot wait for exact answers to the questions posed above. As long as the actual influences to which the vulcanizate is exposed in service are not known, just so long must one make the best of other methods in order to be able to draw some conclusions and to achieve some progress in the testing technique for compound development. There are three possibilities in this direction.

COMPOUND DEVELOPMENT FOR THROWING LIGHT ON SERVICE REQUIREMENTS

For the preparation of an article, different compounds can be employed, which differ from each other particularly in the properties that are important for a definite requirement. In this connection, qualities with the strongest possible differentiation must be selected, even if, for other reasons, there may be no intention of using them later. The first compound development must be undertaken for the sake of throwing light on the required properties in the interest of a later detailed development. Naturally it would be ideal if the compounds which are to be compared were to differ only in the characteristic that is to be studied, but this is hardly likely to be the case.

PHYSICAL ANALYSIS OF PROVEN REPRESENTATIVE TYPES

It may happen there are already available representative types that meet, or have at some time met, the demands of practice better than the same article when this is constructed with other compounds. Of course there must be some assurance that the service conditions were unchanged, on the average, over a rather long time, in case the articles were not together in service simultaneously. It must again be presupposed that one has some idea of the necessary characteristics, and painstaking testing must above all take these characteristics into account. If the preconceptions are correct, then this physical analysis must make it possible to find a clear difference between the two materials, or else the test methods are to be progressively improved until a decisive difference can be obtained. Then the ensuing compound development must attempt to secure these properties of the material which has already proved itself to be satisfactory. The testing of the compounds so developed should, of course, make use principally of those methods which revealed the large difference.

CHANGES IN PROPERTIES DURING SERVICE

Since long before complete destruction there is already a loosening of the binding mechanisms, it is assumed that the effect of service conditions is to

bring about a gradual change of the properties of the material. This incipient damage must lead to a falling off in the decisive properties. The alteration of properties can be considered as a guide to the nature of the service conditions, and used as a criterion for the laboratory testing. Thus Buist⁴ has investigated the time dependence of abrasion on the road and compared it with the laboratory abrasion results. He found that, in one case, the rate of wear decreases with time, in the other the opposite is true, and he proposed that the laboratory tests be modified progressively until the course of the test process should become at least similar to that in the road abrasion.

Williams, Hannel, and Swanson⁴ investigated the change of tensile strength of the cord during the time of running in a tire in road tests by removing cords from different portions of tires that had run for various times and testing them. They found that, especially in the flexed zone of the tire wall and in the inner layers of the tire, there was a pronounced linear decrease of tensile strength with the running time of the tire. This analysis shows that the linear decrease of tensile strength of the cord must be closely related to its fatigue in the tire. The investigation of the change in tensile strength of cords after being subjected to various treatments in cord fatigue testers is, therefore, a criterion useful in the development of a cord-fatigue testing program. The authors made a study of various test apparatus and found that the only one capable of reproducing the decrease of tensile strength of the cord and of arranging the different types of apparatus in the same order of merit as that found in tires was a modified Goodrich compression fatigue tester. The modification was the intensifying of the test pressure.

SUMMARY

A critical consideration shows that the test methods in current use for vulcanizates often fail to make possible a reliable decision about different rubber compounds out of a series of development formulations with respect to their evaluation for subsequent use. The tester by himself is not in a position to bring about an improvement in this unsatisfactory state of affairs, since this cannot be accomplished by the improvement of existing methods alone or by the creation of a new apparatus. A closer cooperation between the fields of testing and application is necessary.

REFERENCES

- ¹ ASTM Standards 523-41 T.
- ² Alfrey, "Mechanical Behavior of High Polymers," Interscience Publishers, Inc., New York and London, 1948.
- ³ Scheele, *Kautschuk u. Gummi* 5, WT 81 (1952).
- ⁴ Spaeth, *Gummi u. Asbest* 3, 332 (1950).
- ⁵ ASTM Standards D 676-49 T, "Indentation of Rubber by Means of a Durometer".
- ⁶ Soden, "A Practical Manual of Rubber Hardness Testing," MacLaren and Sons, Ltd., London, 1951.
- ⁷ Memmler, "Handbuch der Kautschukwissenschaft", S. Hirzel, Leipzig, 1930.
- ⁸ Boonstra, *Rev. gén. caoutchouc* 27, 7 (1950).
- ⁹ Kainradl, *Gummi u. Asbest* 6, 529 (1953).
- ¹⁰ Busse, *Ind. Eng. Chem.* 26, 1194 (1943).
- ¹¹ Ecker, *Kautschuk u. Gummi* 5, WT 97 (1952).
- ¹² Angioletti, *Kautschuk u. Gummi* 6, WT 171 (1953).
- ¹³ Graves, *India Rubber World* 122, 534 (1950).
- ¹⁴ Dillon and Gehman, *India Rubber World* 115, 61, 217 (1946).
- ¹⁵ Marvin, "Report of the National Bureau of Standards on the Cooperative Program on Dynamic Testing," April 1951.
- ¹⁶ Kainradl and Haendler, *Kautschuk u. Gummi* 5, WT 3 (1952).
- ¹⁷ Hopkins, *RUBBER CHEM. AND TECHNOL.* 24, 507 (1951).
- ¹⁸ Oberto and Palandri, *Rubber Age* 63, 725 (1948).
- ¹⁹ Kainradl and Haendler, *Kautschuk u. Gummi* 7, WT 1, 34 (1954).
- ²⁰ Krug, *Kautschuk u. Gummi* 5, WT 72 (1952).
- ²¹ Kickstein, *Kautschuk u. Gummi* 7, WT 50 (1954).
- ²² Wolf, *Kunststoffe* 41, 89 (1951).

- ²⁸ Fisher, "Statistical Methods for Research Workers", Oliver and Boyd, London, 1950; "The Design of Experiments", Oliver and Boyd, London, 1951; Davies, "Statistical Methods in Research and Production", Oliver and Boyd, London, 1949; Linder, "Statistische Methoden fuer Naturwissenschaftler, Mediziner, und Ingenieure", Birkhauser, Basel, 1951; Graf and Henning, "Statistische Methoden bei Textil-Untersuchungen", Springer, Berlin/Goettingen/Heidelberg, 1952.
- ²⁹ International Organization for Standardization, ISO Technical Committee 45—Rubber, "Interlaboratory Comparison of Tests on the Du Pont Abrasion Test", Report No. 105, July 1951.
- ³⁰ Mandel, Steel, and Etiehler, *Ind. Eng. Chem.* **43**, 2901 (1951).
- ³¹ Buist and Davies, *Trans. Inst. Rubber Ind.* **22**, 68 (1946); *RUBBER CHEM. AND TECHNOL.* **20**, 294 (1947).
- ³² Thornley, *Trans. Inst. Rubber Ind.* **24**, 241 (1949).
- ³³ Budd and Larrik, *ASTM Bull. No.* **136**, 19 (1945).
- ³⁴ International Organization for Standardization, ISO Technical Committee 45—Rubber, "Draft ISO Proposal for Du Pont Method of Measuring Abrasion Resistance", Report No. 99, April 1951.
- ³⁵ Schneider, *Kautschuk u. Gummi* **6**, WT 111 (1953).
- ³⁶ Fachler and Rugg, *RUBBER CHEM. AND TECHNOL.* **25**, 331 (1952).
- ³⁷ ASTM Standards D 430-51T, "Dynamic Testing for Ply Separation and Cracking of Rubber Products".
- ³⁸ ASTM Standards D 813-52 I, "Resistance of Vulcanized Rubber or Synthetic Elastomers to Crack Growth".
- ³⁹ "Out-door Flexing Machine", in the *Vanderbilt Rubber Handbook 1948*.
- ⁴⁰ British Standards 903; Part 26, 1950, "Resistance to Flex Cracking and Cut Growth".
- ⁴¹ Newton, *Trans. Inst. Rubber Ind.* **15**, 172 (1939).
- ⁴² Ford and Cooper, *India Rubber World* **124**, 695 (1951); **125**, 55 (1951).
- ⁴³ Kuzminskii, *RUBBER CHEM. AND TECHNOL.* **24**, 250 (1951).
- ⁴⁴ Oppel, *Automobiltechn.-Z.* **51**, 1 (1949).
- ⁴⁵ Kern, *Kautschuk u. Gummi* **6**, WT 178 (1953).
- ⁴⁶ Loughborough, Davies, and Monfore, *Can. J. Res., Sect. 28*, 490 (1950).
- ⁴⁷ Brunner, *Deutsch. Kraftfahrtforsch.* **2**, 1 (1938).
- ⁴⁸ Buist, *Engineering*, Feb. 8, 1952.
- ⁴⁹ Williams, Hannel, and Swanson, *Ind. Eng. Chem.* **45**, 796 (1953).
- ⁵⁰ ASTM Standards D 624-48.

DETERMINATION OF SULFUR BY WET COMBUSTION WITH PERCHLORIC ACID *

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In this institute the sulfur content of wood and pulp samples has hitherto been determined by the method of Grote and Krekeler¹. The sulfur content of these samples is sometimes fairly low, of the order of 1 per cent or less, so that 1 gram or more is required for each analysis. This leads to lengthy combustions. In some samples the considerable ash content made the combustion tubes become opaque so that they had to be frequently replaced, leading to increased costs.

Because of these disadvantages it was decided to try wet combustion techniques for wood and pulp samples. First a method described by Klingstedt² was applied to pure organic substances, such as sulfosalicylic acid and thiourea; the results were often low and the length of time required for digestion, 2 to 4 hours, was considered disadvantageous. When the resulting solution was evaporated to dryness, a more or less black residue, obviously containing charred decomposition products, was sometimes obtained, an indication that the oxidation was not complete.

With this experience in mind, attention was turned to methods using perchloric acid for the wet combustion. Such methods for the determination of sulfur have been described by Kahane and coworkers, first in a method applicable to vulcanized rubber³ and later for samples of biological origin⁴. These methods were developed further by Wolesensky⁵ and Smith⁶ for the determination of sulfur in coal and in 1934 Kahane and Kahane⁷ described a general method for determining sulfur in organic substances.

Preliminary experiments in this institute confirmed the observation of Kahane that sulfur-containing gases escape if the wet decomposition with perchloric acid is done in open vessels. The escaping gas is presumably sulfur dioxide, as no hydrogen sulfide could be detected.

According to Staudinger and Niessen⁸, carbonyl sulfide may be formed in some cases. This substance is a relatively stable gas, and it is possible that it escapes when the oxidation is carried out in an open vessel.

The experiments were continued with the apparatus previously described⁹ (Figure 1). When this apparatus was used, recoveries of sulfur were quantitative (see Tables III and IV), even when iodic acid was omitted, so it was considered superior to the one described by Kahane.

After the wet combustion, the reaction flask contains a mixture of perchloric acid and the sulfuric acid to be determined, together with a small amount of nitric acid and the decomposition products of perchloric acid. After dilution with water, it is possible to determine the sulfate content direct by precipitation with barium chloride solution. This procedure is, however, time-consuming and laborious, and it would be more desirable to transform the sulfur into

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hydrogen sulfide. This may be accurately determined by volumetric or colorimetric methods, which are much more sensitive than gravimetric methods for the determination of sulfate.

Boiling with a reducing mixture containing hydriodic acid as a method of reducing sulfates to sulfides was proposed by Lorant¹⁰, and this technique has been further developed for analytical purpose by Luke¹¹, Roth¹², and Johnson and Nishita¹³. The method of Luke¹¹ for the determination of sulfur in rubber was of special interest because here reduction takes place in the presence of perchloric acid. This would appear to involve great risk of explosion. Experiments showed, however, that when the reducing mixture of Luke, which contains hydriodic, hypophosphorous, and hydrochloric acids, was boiled with

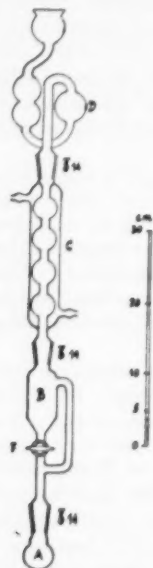


FIG. 1.—Wet decomposition apparatus.

perchloric acid in the proportion 3 to 1, there was no tendency to violent reaction; in fact, no reaction at all took place. When the experiment was repeated with mixtures containing more perchloric acid, a slow formation of iodine was obtained. It is obvious that if the reducing mixture is boiled with perchloric acid in the proportion 3 to 1, the temperature, about 120° C, is so low that the oxidizing properties of perchloric acid do not appear. In wet decomposition experiments, the oxidizing properties of perchloric acid begin to be noticeable at about 150° to 180° C. Having carried out thousands of sulfur determinations, the author is convinced that there is no risk of violent reaction in boiling perchloric acid with the reducing mixture in the stated proportions.

When the reducing mixture was added directly to the mixture in the reaction flask after the wet decomposition, in order to boil off the hydrogen sulfide, some difficulties arose. Residual nitric acid and other oxidizing substances such as chlorine caused a formation of free iodine, which reacted with the hydrogen sulfide already formed. Hydrobromic acid, which reduces nitric acid and other

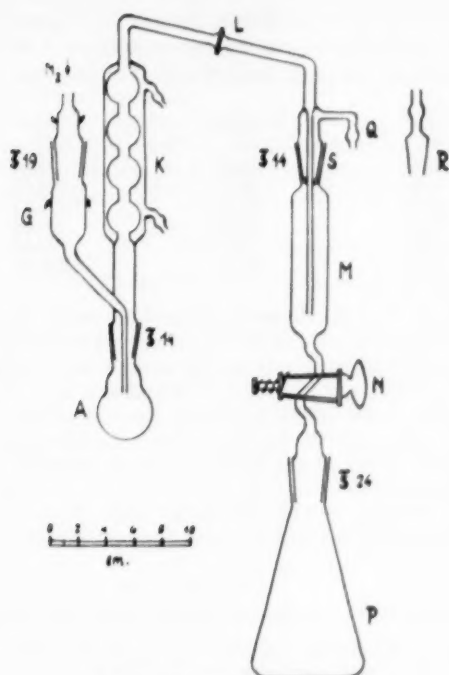


FIG. 2.—Apparatus for reduction.

oxidizing substances formed without affecting the sulfuric or the perchloric acid, was found to be a most suitable reagent for destroying these substances. After this treatment, the hydrogen sulfide could be boiled off without any formation of iodine.

The quantitative experiments on the reduction of sulfuric acid to hydrogen sulfide were carried out in the apparatus shown in Figure 2. In order to avoid any oxidation of the hydrogen sulfide formed, nitrogen, previously freed from oxygen by the method of Meyer and Ronge¹⁴, was used as carrier gas. Although no abnormal results were obtained when nitrogen was used without prior purification, it seemed wise to standardize the purification procedure, since the quality of the nitrogen may vary in different gas cylinders. In order

TABLE I
REDUCTION OF POTASSIUM SULFATE WITHOUT ADDITIONS
(Theoretical, 18.38% S)

Amount taken (mg.)	S found (%)	Yield (%)
9.96	18.37	99.95
10.10	18.39	100.05
11.19	18.41	100.16
11.96	18.39	100.05
11.71	18.39	100.05
11.40	18.43	100.27

TABLE II
REDUCTION OF POTASSIUM SULFATE
(Hydrobromic acid and perchloric acid added. Theoretical, 18.38% S)

Amount taken (mg.)	S found (%)	Yield (%)
12.33	18.29	99.51
9.26	18.41	100.16
11.71	18.44	100.33
10.91	18.20	99.02
11.01	18.41	100.16
9.78	18.38	100.00

to reduce the amount of hydriodic and hydrochloric acids carried over into the receiver, water cooling was introduced, but it proved unnecessary to scrub the gas with water or dilute hydrochloric acid to remove acid fumes. The amount of these carried over during a 15-minute distillation is more than neutralized if the receiver contains 20 ml. of 3*N* sodium hydroxide solution. As the gases escaping from the apparatus are harmless, it can be operated on an open laboratory bench. The design of the receiver and the titration of the hydrogen sulfide have been described¹⁸.

To ensure quantitative recovery of sulfur with the reduction mixture of Luke, experiments were carried out in which dried potassium sulfate was boiled

TABLE III
INFLUENCE OF SOME ADDITIONS BEFORE WET DECOMPOSITION
Variations. 1. According to procedure given for semimicro-samples
2. Preoxidation with NaOH + H₂O₂
3. Preoxidation with Br₂ + H₂O₂
4. 500 mg. of glucose added
5. Ammonium chromate added

Variation	Substance	Amount taken (mg.)	% S Theoretical	% S Found
1	Taurine	10.31	25.63	7.48
1		9.22		11.44
2		9.50		7.73
2		9.08		21.50
3		9.38		25.77
3		10.32		25.75
4		9.73		25.67
4		9.55		25.56
5		10.02		25.77
5		9.68		25.76
1	Sulfonal	11.98	28.09	26.23
3		10.82		25.29
3		9.33		26.83
4		9.32		26.13
5		10.04		28.20
5		13.20		28.12
5		13.59		28.25
1		15.23	10.92	4.36
3		16.84		6.65
4		15.55		10.76
4		16.97		11.04
4		14.12		10.89
5		14.46		10.98
4 + 5		13.43		10.90

with 7 ml. of the reduction mixture in the apparatus mentioned. The results are given in Table I. As these results were encouraging, similar experiments involving the addition of 2 ml. of perchloric acid and pretreatment with hydrobromic acid (see below) were carried out. In view of the success of these experiments (Table II), determinations of sulfur in organic substances were attempted. The final procedure for semimicro-samples is given below. With this procedure the results became quantitative, the recoveries being between 98 and 101 per cent (see Table IV).

TABLE IV
TYPICAL EXAMPLES, ANALYSIS OF PURE SAMPLES

Substance	Amount taken (mg.)	% S Theoretical	% S Found	Yield (%)
Sulfosalicylic acid	21.89	12.62	12.66	100.3
	22.21		12.66	100.3
Thiourea	19.92	42.13	42.13	100.0
	22.69		41.60	98.7
1-Cystine	20.43	26.70	26.71	100.0
	20.59		26.56	99.5
Mercaptobenzothiazole	18.09	38.34	38.92	101.5
	19.48		37.99	99.1
<i>p</i> -Toluenesulfonyl chloride	22.46	16.82	16.69	99.2
<i>p</i> -Bromosulfonylanisidine	28.57	9.37	9.43	100.6
	22.62		9.42	100.5
1 (4-Methoxyphenyl)-propane-2-sulfonic acid, Ba salt	19.12	10.76	10.82	100.6
1-Phenyl-3-hydroxypropane-2-sulfonic acid, Ba salt	14.82	11.29	11.32	100.3
Sulfur	9.03	100.0	101.4	101.4
Barium sulfate	20.15	13.72	13.62	99.2
Potassium sulfate, see Tables I and II				
Benzyl disulfide	60.00	26.03	25.69	98.7
	11.84		25.89	99.5
<i>s</i> -Benzylthiouronium chloride	12.50	15.82	15.87	100.3
	10.69		15.91	99.9
Phenylthiourea	11.38	21.07	21.10	100.1
	11.69		21.02	99.8

APPARATUS

Wet decomposition apparatus (Figure 1)¹⁶.

Apparatus for determination of hydrogen sulfide (Figure 2). The apparatus is made of borosilicate glass with standard-taper joints; the ball and socket joint, *L*, has been introduced to reduce strains when handling the apparatus. The absorption vessel, *M*, and the titration flask, *P*, have been described¹⁶. It is essential that the titration flask be made of extra-thick glass, to avoid explosions. The size of reaction flask *A* is not critical, and for semimicro-samples 50-ml. flasks can be used. When flask *P* is to be evacuated, mouthpiece *R* is connected to a water suction pump and inserted into joint *S*. The apparatus is easily cleaned by pouring acetone into funnel *G* and connecting *Q* to the suction pump¹⁷.

REAGENTS

Acid mixture for wet decomposition, 40 ml. of perchloric acid, $d = 1.69$, and 60 ml. of nitric acid, $d = 1.40$.

Hydrobromic acid, $d = 1.49$.

Reduction mixture. Hydriodic acid (160 ml.), $d = 1.70$, 45 ml. of hypophosphorous acid (H_3PO_2) (50%), and 160 ml. of hydrochloric acid, $d = 1.19$, are refluxed for 1 hour. Nitrogen or carbon dioxide should be passed through the mixture during this operation.

Sodium hydroxide solution, 3*N*, 120 grams of sodium hydroxide per liter.

Phosphoric acid, 5*M*, phosphoric acid (342 ml.), $d = 1.74$, is diluted to 1 liter.

Iodine solution, about 0.01*N*.

Sodium thiosulfate solution, standardized 0.01*N*.

PROCEDURE FOR SEMIMICRO-SAMPLES

The sample is weighed into a 50-ml. flask, *A*, provided with a No. 14 tapered joint. Five ml. of the acid mixture for wet decomposition is introduced into the reflux receiver, *B* (Figure 1), with stopcock *F* closed. The condenser, *C*, the flask, *A*, and the scrubber, *D*, are mounted according to the figure. The scrubber is filled with a few ml. of water or 3 per cent hydrogen peroxide solution. Stopcock *F* is opened and, if necessary, flask *A* is heated with a microburner until nitrous fumes begin to form. After heating for 5 minutes, stopcock *F* is closed and heating is then continued until all the nitric acid has been collected in *B* and dense fumes of perchloric acid are formed in the reaction flask. The heating is moderated so that no fumes are allowed to pass through condenser *C*.

When the sample is completely oxidized, the apparatus is left for a few minutes to cool slightly. Stopcock *F* is opened and the liquid in *B* is allowed to flow into *A*. The solution is boiled for a minute to rinse the apparatus, *F* is then closed, and most of the nitric acid is distilled into *B* until the first fumes of perchloric acid appear in *A*. The apparatus is then allowed to cool.

Reaction flask *A* is removed and 8 ml. of hydrobromic acid are added. The flask is heated gently while bromine gas is leaving the flask and until the contents is light brown. If a stream of inert gas is passed through the flask, this procedure is accelerated.

The apparatus for the determination of hydrogen sulfide (Figure 2) is now made ready. Fifteen ml. of 5*M* phosphoric acid are introduced into titration flask *P*, and absorption vessel *M* with stopcock *N* open is inserted into the neck of the titration flask, which is then evacuated through mouthpiece *R*. Stopcock *N* is closed, *R* is removed, and the titration flask with the absorption vessel, now filled with 20 ml. of 3*N* sodium hydroxide solution, is connected to the apparatus at *S*. Seven ml. of the reduction mixture is added to the contents of flask *A*, which is immediately connected to the apparatus. A moderate stream of oxygen-free nitrogen is passed through the apparatus, and the mixture in *A* is boiled for 15 minutes. All the hydrogen sulfide is now driven over and stopcock *N* is opened slowly, so that the adsorption solution flows down into the titration flask. Joint *S* is disconnected, and *M* is rinsed with a little water, which is also sucked down into *P*. Fifteen ml. of iodine solution is pipetted into *M* and sucked down. After being rinsed, assembly *MNP* is shaken vigorously for 1 minute. If all the iodine is consumed, more is added and the shaking is repeated. When there is an excess of iodine in the titration vessel, the vacuum is released and absorption vessel *M* is removed. The excess iodine is back-titrated with standardized sodium thiosulfate solution, using starch solution as indicator.

CALCULATION

a = ml. of thiosulfate solution consumed

b = ml. of thiosulfate solution consumed by an amount of iodine solution equal to that added to the titration flask

n = normality of the thiosulfate solution

w = mg. of sample taken

Percentage of sulfur. $\% S = 1603(b - a)n/w$

DISCUSSION

The main difference between wet combustion by this method and that of Kahane is the use of an apparatus which makes the addition of iodic acid unnecessary. In this apparatus, contact between the gases evolved during the combustion is better, so that the nitrogen dioxide initially formed fills the reflux receiver and remains there during the whole operation. All the sulfur dioxide, even that which may form during the later stages, coming into contact with the nitrogen dioxide forms sulfuric acid, which condenses on the inside walls of the apparatus and is brought down into the reaction flask during the second refluxing operation.

The time necessary for the complete oxidation of the sample depends on its nature but, in general, 10 minutes of boiling of the perchloric acid is sufficient. The reaction time can be determined if potassium chromate is added as an indicator, as proposed by Smith¹⁸.

Some organic substances, usually of low molecular weight, have been reported as being resistant to oxidation by perchloric acid. Among sulfur-containing substances of this type, Balks and Wehrmann¹⁹ have found that taurine and thioglycollic acid are not completely oxidized by hot perchloric acid. They recommend that the substance be preoxidized by treatment with alkaline bromine solution or that a more easily oxidizable substance, such as starch, be added to the sample. Jones²⁰ has found that sulfonyl is of the same type and that this substance is not oxidized even after pretreatment with aqua regia. The author has found that the barium salt of sulfoacetic acid is also of this type.

When the semimicromethod described was applied to these substances, in agreement with the previous authors it was found that the observed values for sulfur were low and irregular. Different methods of obtaining quantitative recoveries of sulfur were investigated, and the results of these experiments are listed in Table III. Four variations (methods 2 to 5) of the basic procedure (method 1) were tried. Of special interest is the fact that the use of catalysts, as recommended by Smith¹⁸, gives good results in all cases, and the catalyst does not interfere with the conversion of sulfate into sulfide.

Theoretical values were obtained when trimethylenethiourea, which gives carbonyl sulfide on oxidation with nitric acid², was determined according to this method: (theory, 27.59; found, 27.39 and 27.66 per cent). This shows that this type of substance can be analyzed without special precautions.

When the sulfur content of inorganic substances is to be determined, it is sometimes unnecessary to carry out the wet combustion. Sulfates, sulfites, and sulfides give up all their sulfur as hydrogen sulfide on boiling with the reduction mixture, but elementary sulfur does not. In the case of sulfites and thiosulfates, an alkaline preoxidation is recommended to avoid losses due to formation in the cold of large quantities of sulfur dioxide.

The presence of barium in the sample does not involve any difficulty, although it may sometimes be wise to increase reduction time to 30 minutes. However, in the case of inorganic samples, it is better to treat the sample with 2 ml. of hot perchloric acid before reduction in order to dissolve the barium sulfate. When the reduction mixture is added, the barium sulfate is reprecipitated in a finely divided form, which reacts easily with the reduction mixture. After reduction is complete, there should be no precipitate left in the reaction flask.

Some typical determinations on diverse pure substances, organic and inorganic, are given in Table IV.

BIOLOGICAL AND TECHNICAL SAMPLES

The main purpose of this investigation was not to find a new semimicro-technique for the determination of sulfur in pure, organic substances, since many such methods exist. However, the fact that the recoveries of sulfur are quantitative for a great number of pure compounds shows that the method can be safely applied to substances of biological and technical origin.

When technical or biological materials are to be analyzed, the sample weight often has to be increased for two reasons: The sulfur content may be rather low, of the order of 1 per cent or less, or the material may not be homogeneous, so that a sample of 0.5 gram or more must be taken in order to get reproducible results.

It is on products of this kind that the wet combustion technique would be expected to have many advantages, compared to dry combustion methods. However, the procedure cannot be made as general as the one for semimicro-samples, and it must be varied to suit the individual case. An injudicious use of perchloric acid may lead to violent reaction, but if some simple rules are followed, this risk can be eliminated.

The reaction of perchloric acid with organic substances has been studied by Smith¹⁸, and in a recent paper by Kahane²¹ a review is given of its applications in analytical chemistry. In both these papers the risks attending the use of perchloric acid are discussed. In the special case of sulfur determination it seems safe to decompose the sample with a mixture of nitric and perchloric acids, since the nitric acid destroys all the easily oxidizable substances, leaving only a residue of material more resistant to the perchloric acid. When nitric acid is used, the temperature of the acid mixture rises slowly and smoothly, so that the oxidizing power of the perchloric acid is gradually increased, thereby effecting a progressive breakdown of the sample. If a new substance or material is to be investigated a small sample, 50 mg. or so should be decomposed by the semimicro-method, and if the decomposition proceeds without charring or excessive foaming, the sample weight can be increased. If charring occurs, the amount of nitric acid can be increased or the time for reflux boiling prolonged. The use of catalysts according to Smith¹⁸ may speed up the procedure appreciably.

For example, when samples of wood are to be decomposed, 5 ml. of the acid mixture and an additional 5 ml. of nitric acid are used for decomposition. The reaction flask is heated a little until a reaction starts, giving rise to large amounts of nitrous gases. When this reaction has subsided, the sample is dissolved, and the procedure given for semimicro-samples is followed. When the nitric acid is almost driven over into the reflux collector, the flame is moderated so

that the perchloric acid does not react too rapidly, thereby driving fumes of perchloric acid out of the apparatus.

These directions for wood samples can be followed with only minor modifications for most types of plant material. The amounts of hydrobromic acid and reduction mixture should be chosen so that the proportions remain the same as those in the semimicroprocedure. However, if extra nitric acid is added, there is no need to increase these quantities, since the amount of perchloric acid left in the reaction flask is unchanged.

The method has also been applied to a few samples of technical products of other kinds. Samples of leather, coal, rubber, plastics, hair, light concrete, and mortar were analyzed. Some of the results are listed in Table V. These samples have been analyzed mainly as described for wood samples; in the case of concrete and mortar, the same results were obtained if the wet decomposition was omitted. The method should be suitable for all materials that can be de-

TABLE V
SOME EXAMPLES, ANALYSIS OF TECHNICAL PRODUCTS

Substance	Amount taken (mg.)	% S Found	% S Expected
Rubber D-0	60.07	0.831	0.79
Rubber D-1	66.89	0.785	0.79
Rubber D-2	90.40	0.782	0.79
Poly(methyl methacrylate)	1081	0.064	0.06
	945.5	0.063	0.06
Leather 031154	194.77	1.61	1.50
	136.90	1.61	1.50
Calves' hair	263.0	3.77	3.66
Light concrete	69.28	2.12	2.4
	69.40	2.10	2.4
Mortar, weathered	98.54	1.25	—

composed by wet decomposition. In the case of aqueous solutions it is wise to add some hydrogen peroxide to the sample, so that neither hydrogen sulfide nor sulfur dioxide may escape before the concentration of nitric acid has reached an oxidizing level.

SUMMARY

Difficulties in the determination of sulfur in wood and pulp samples by the conventional method of Grote and Krekeler have been overcome by applying a wet combustion technique, using perchloric and nitric acids. The sulfur is reduced to hydrogen sulfide by boiling with a reduction mixture, and determined iodometrically. The method gives quantitative yields for pure organic compounds, and is suitable for a great variety of samples with sulfur contents from 0.01 to 100 per cent. Sample weights can be varied from 9 mg. to 5 grams.

ACKNOWLEDGMENT

The author thanks Rose Marie Persson for great help in carrying out analyses and John Haslam, Sven Jennerholm, and Günther Niessen for providing samples.

REFERENCES

- ¹ Grote and Krekeler, *Angew. Chem.* **46**, 106 (1933).
- ² Klingstedt, *Z. Anal. Chem.* **112**, 101 (1938).
- ³ Kahane, *Caoutchouc et Gutta-percha* **24**, 13549 (1927).
- ⁴ Lematte, Boinot, and Kahane, *Compt. Rend. Soc. Biol.* **96**, 1211 (1927).
- ⁵ Wolesensky, *Ind. Eng. Chem.* **20**, 1234 (1928).
- ⁶ Smith and Deem, *Ind. Eng. Chem. Anal. Ed.* **4**, 227 (1932).
- ⁷ Kahane and Kahane, *Bull. Soc. Chim.* **1**, 280 (1934).
- ⁸ Staudinger and Niemen, *Chem. Ber.* **9**, 1223 (1953).
- ⁹ Bethge, *Anal. Chim. Acta* **9**, 129 (1953).
- ¹⁰ Lorant, *Z. Physiol. Chem.* **185**, 245 (1929).
- ¹¹ Luke, *Ind. Eng. Chem. Anal. Ed.* **15**, 602 (1943).
- ¹² Roth, *Mikrochemie per. Mikrochim. Acta* **36-37**, 379 (1951).
- ¹³ Johnson and Nishita, *Anal. Chem.* **24**, 736 (1952).
- ¹⁴ Meyer and Ronge, *Angew. Chem.* **52**, 637 (1939).
- ¹⁵ Bethge, *Anal. Chim. Acta* **9**, 129 (1953).
- ¹⁶ For details, see Bethge, *Anal. Chim. Acta* **9**, 129 (1953).
- ¹⁷ Both sets of apparatus are obtainable from Firma Werner Glas, Slöjdgatan 1, Stockholm C, Sweden.
- ¹⁸ Smith, *Anal. Chim. Acta* **8**, 397 (1953).
- ¹⁹ Balks and Wehrmann, *Bodenkunde u. Pflanzenernähr.* **5**, 48 (1937).
- ²⁰ Jones, *J. Assoc. Offic. Agr. Chemists* **26**, 182 (1943).
- ²¹ Kahane, *Oesterr. Chem.-Ztg.* **55**, 209 (1954).

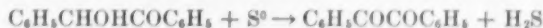
SPOT TEST REACTION FOR THE DETECTION OF ELEMENTAL SULFUR *

FRITZ FEIGL AND CECILE STARK

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Various procedures have been recommended for the spot test detection of elementary sulfur in solid materials or dissolved in organic liquids¹. These tests are reliable and some of them are very sensitive; however, they are not particularly rapid. None of them involves the formation of hydrogen sulfide from the sulfur, a product which can be detected with high specificity and sensitivity. A convenient formation of hydrogen sulfide from sulfur is found in a study by Zymaczynski² of a macro-test for free sulfur and several ketonic alcohols. The basis of the test is that glycerol containing iron yields black iron sulfide when heated with sulfur and ketonic alcohols. (The reagent is prepared by allowing glycerol to stand with iron filings for several weeks with access to air.) Zymaczynski states that 0.1 mg. of sulfur dissolved in 1 ml. of such glycerol can be detected if 1 ml. of glycerol containing 5 to 10 mg. of ketonic alcohol is added and the mixture is heated over a free flame.

The chemical basis of the test is that an oxidation-reduction reaction between sulfur and the ketonic alcohol produces hydrogen sulfide, which in turn yields iron sulfide with the iron contained in the reagent. Zymaczynski offers as proof of this interpretation that much hydrogen sulfide is released when 10 mg. of sulfur is heated with 70 mg. of benzoin. Accordingly, the oxidation-reduction reaction in this case would lead to the formation of benzil and hydrogen sulfide:



This test for sulfur was checked with respect to its applicability in spot test analysis, and it was found that the production of iron sulfide in glycerol cannot be recommended. On the other hand, the authors have observed that direct fusion with benzoin (melting point 137° C) at 140° to 150° C provides a very sensitive and rapid test for free sulfur, since the hydrogen sulfide formed can be readily detected by the simple procedures of spot test analysis.

PROCEDURE

The test is conducted in a micro test-tube (5 × 0.5 cm.). A few grains of the solid sample, or 1 to 3 drops of a solution in carbon disulfide, benzene, etc., evaporated to dryness, suffice. Several hundredths of a gram of benzoin is added, the mixture is stirred with a glass rod if necessary, and the open end of the test-tube is covered with a disk of moist lead acetate paper. The tube is then plunged into a glycerol bath previously heated to 130° C, and the temperature is raised to between 140° and 150° C. Depending on the quantity of free sulfur in the sample, a black or brown stain appears on the reagent paper at once or within 1 to 2 minutes.

* Reprinted from *Analytical Chemistry*, Vol. 27, No. 11, page 1838, November 1955.

When testing for sulfur dissolved in low-boiling solvents, it is best to place the benzoin in the test-tube first and then to add a drop or two of the solution. The test-tube should then be carefully warmed by suspending it in the glycerol bath, whose temperature is gradually raised.

LIMIT OF IDENTIFICATION, 0.5 γ

This procedure is adequate for the majority of instances in which it is necessary to detect the presence of free sulfur. A greater sensitivity is attained by the use of a capillary tube, the open end of which is closed, after introducing the charge, with a loose plug of cotton moistened with lead acetate solution.

The test was tried on agricultural insecticides, pharmaceutical preparations, black gunpowder, match heads, vulcanized rubber, and gas purification material. The results were excellent.

Selenium does not undergo a similar oxidation-reduction reaction with benzoin. Neither does it interfere with the tests for sulfur. A satisfactory response was obtained with a mixture of 10 γ of sulfur and 25 mg. of selenium (1 to 2500).

The fusion reaction with sulfur can be reversed and thus serve for the detection of benzoin. This procedure can be used for the detection of many compounds containing the secondary alcohol group. A detailed report of this finding will be given later.

SUMMARY

Hydrogen sulfide is formed when free sulfur is heated with fused benzoin. This is the basis of a new and sensitive test for free sulfur in mixtures with organic or inorganic substances. The heating is done in a test-tube, whose mouth carries lead acetate paper. The limit of identification is 0.5 μ . Selenium does not interfere. Tests of a wide variety of commercial products gave satisfactory results.

REFERENCES

- ¹ Feigl, "Spot Tests", Elsevier Publishing Co., New York, 4th Ed., 1954, Vol. 1, p. 334; Vol. 2, pp. 334 and 336.
² Zymacynski, *Z. anal. Chem.* 106, 32 (1936).

ABRASION AND SLIPPAGE

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A CORRECTION

RUBBER CHEMISTRY AND TECHNOLOGY, Volume 28, No. 4, pages 1082-1095, October-December 1955, contains a paper of the title above.

On page 1095, Figure 15 states in its descriptive legend that the ordinate of the diagram represents the *S* value; the legend on the figure itself indicates no function (-Werte).

The ordinate of Figure 15 actually represents the *L* value, as stated in the text in the sentence beginning four lines below Figures 14 and 15.

RUBBER CHEMISTRY AND TECHNOLOGY is grateful to the senior author, Dr. G. Ebert, for calling attention to this error.

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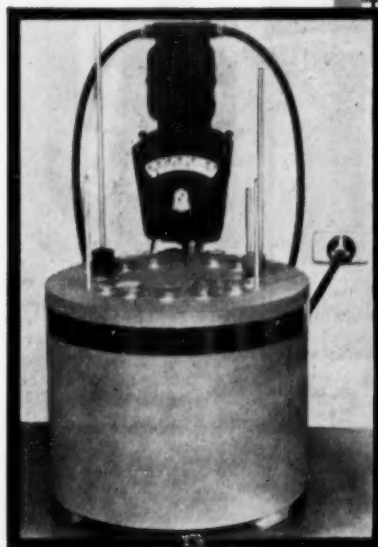
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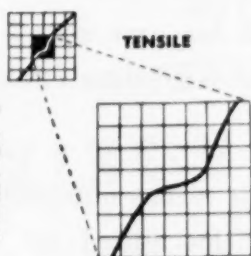
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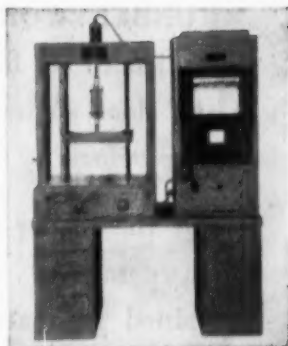
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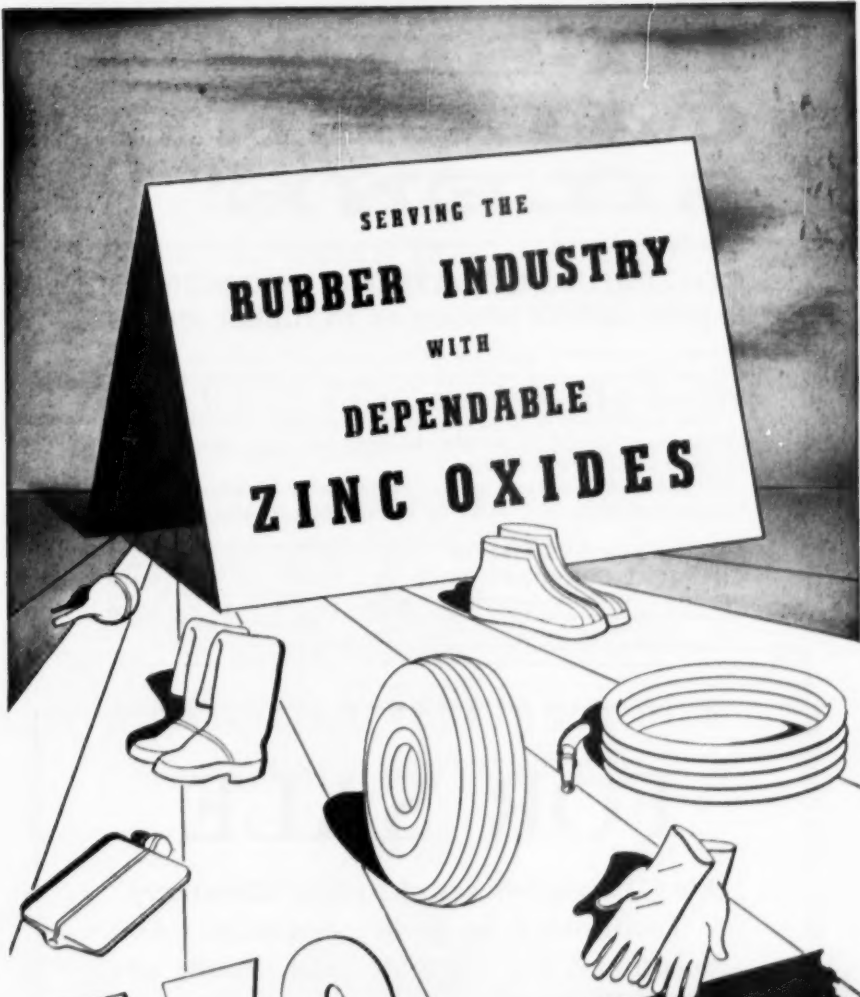
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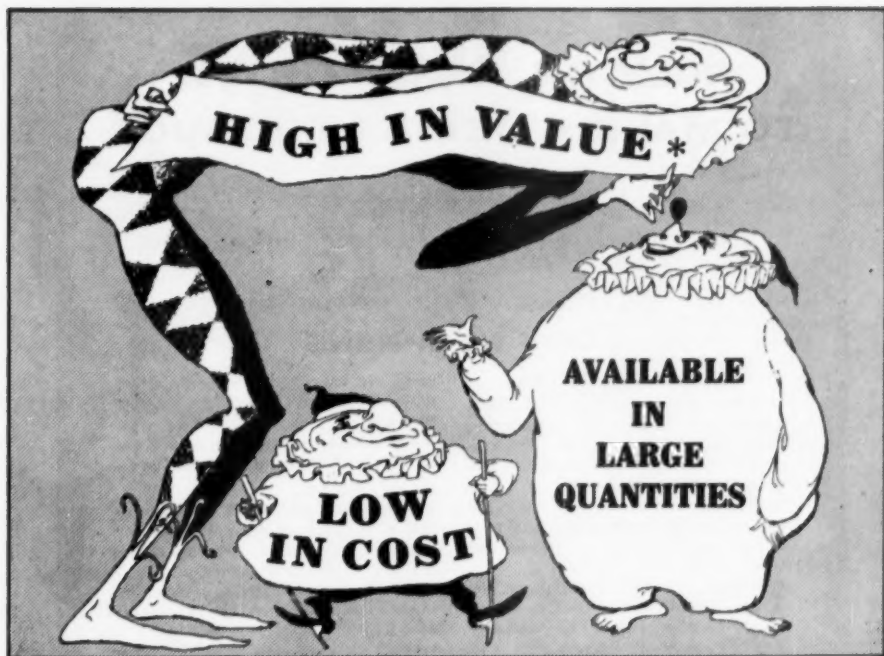
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